CIS 2019
Industry Society Chemistry

Chemistry meets Industry and Society

A creative showcase conference

Organized by

Società Chimica Italiana

Grand Hotel Salerno
August 28th-30th 2019, Salerno IT

Conference Proceedings

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SUMMARY

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La Chimica e l'Industria (Chemistry and Industry) is a ***one hundred years old*** journal of science & technology and information for chemists.
Founded in 1919 with the original name *Giornale di Chimica industriale*, *La Chimica e l'Industria* has since been the official magazine of *Società Chimica Italiana* (SCI). It hosts articles or short communications in Italian or English on topics of relevant interest to all those working in chemistry.
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CnS - La Chimica nella scuola

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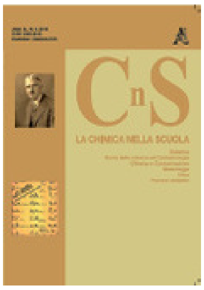

CnS-La Chimica nella Scuola (CnS-Chemistry in the School) aims to provide a scientific, professional and technical aid for the teaching of chemistry in schools of all types and grades and in universities. It also offers itself as a place of discussion of ideas and educational experiences and where to revive and revisit contributions of history of Science and Chemical Education. Furthermore, it is the official magazine of the SCI Division of Chemical Education.
Direttore responsabile: Luigi Campanella. **Editore:** Aracne editrice int.le S.r.l. via Quarto Negroni, 15, 00072 Ariccia (RM)

Molecole in primo piano

http://www.aracneeditrice.it/index.php/collana.html?col=mpp

Molecole in primo piano (Molecules in the foreground) comes from the collaboration of Aracne Editrice with the Senior Group of Società Chimica Italiana (SCI) aimed to the dissemination of chemical sciences and the deepening of their impact on society. The articles in the series follow two different but complementary guidelines: on one side monographs of non-fiction and dissemination characters; on the other hand, short articles that illustrate in a captivating fashion the different aspects of the influence of chemistry in social and daily activities.
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SCHEMATIC PROGRAM

Wednesday, August 28th						
9:30	13:00	*Registration Desk open*				
15:00	17:30					
General Plenary Session						
11:00	13:00	**General Introductory Session** (in Italian & Open to public) **Tavola Rotonda – Round Table** ***Nessun futuro senza chimica*** ***Creare una sinergia positiva tra chimica, società ed industria***				
13:00	15:00	*Break and Poster view*				
15:00	15:15	**Conference Opening**				
15:15	17:30	**Plenary Session** ***Chemistry meets Industry and Society***				
17:30	19:45	**Poster and Brokerage Session**				
20:15	22:30	*Welcome Reception*				
Thursday, August 29th						
8:30	13:00	*Registration Desk open*				
15:00	17:30					
Workshop Sessions						
9:00	11:00	**WS1**	**WS2**	**WS4**	**WS5**	**WS7**
11:00	11:30	*coffee break*				
11:30	13:00	**WS1**	**WS2**	**WS4**	**WS5**	**WS7**
13:00	15:00	*Break and Poster view*				
15:00	17:30	**WS1**	**WS2**	**WS4**	**WS5**	**WS7**
17:30	19:00	**Poster session: WS1, WS2, WS4, WS5, WS7**				
20:00	22:30	*Conference Dinner*				
Friday, August 30th						
8:30	15:00	*Registration Desk open*				
Workshop Sessions						
9:00	11:00	**WS1**	**WS3**	**WS6**	**WS8**	
11:00	11:30	*coffee break*				
11:30	13:00	**WS1**	**WS3**	**WS6**	**WS8**	
13:00	15:00	*Break and Poster view*				
15:00	17:30	**WS1**	**WS3**	**WS6**	**WS8**	
17:30	19:00	**Poster session: WS3, WS6, WS8**				

Poster panels (1 m large x 2 m high) are available and are labeled with the abstract reference number indicated in the program. Posters (suggested size 70x100 cm) need to be exposed in the morning and removed at the end of poster session.

GENERAL PLENARY SESSION

*The **Società Chimica Italiana** (SCI) promotes the study and advancement of Chemistry and of its applications in the framework of the progress and well-being of humanity*

CIS 2019 aims to be a new breakthrough-type international conference aimed to fill an existing gap between the scientific capabilities of research, and industry and society needs, e.g. from idea to innovation. It aims to be a creative showcase conference, with presentations (from projects, scientists, companies, public agencies, etc.) oriented to present:

- applicable research results (rather than just scientific aspects) in a form where communication to companies and non-experts should be pursued
- specific requests from companies regarding both fundamental and applied aspects that they identify as background for innovation
- strategic aspects of research identified by public agencies to foster competiveness in the area of chemistry and address societal grand challenges.

CIS 2019 wants to show the strategic role of Chemistry to foster progress and innovation, with reference to broad topics such as Energy, Health, Sustainability and Security, Everyday life.

The conference is organized in 3 days (August 28th-30th 2019), with the following format:

August 28th

- A public-open morning (in Italian), dedicated to a Round Table discussing the role and opportunities for chemistry to have a stronger role in addressing societal challenges in a closer interaction with industry;
- An afternoon plenary lecture session introducing relevant challenges;
- A poster and brokerage event where companies, start-up, researchers, investors and stakeholders can meet to explore new opportunities of collaboration and partnership;

August 29th – 30th

- Two full days organized in eight thematic parallel workshops (max 5 parallel sessions per day), with invited & keynote lectures, oral communications and poster presentations.

Social events

August 28th: Welcome Reception
August 29th: Conference Dinner

Tavola Rotonda – Round Table

Nessun futuro senza chimica
Creare una sinergia positiva tra chimica, società ed industria

Coordina

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Giornalista scientifico e scrittore, laureato in chimica, è socio fondatore della Fondazione IDIS-Città della Scienza di Napoli; membro del consiglio scientifico dell'Istituto superiore per la protezione e la ricerca ambientale (ISPRA); membro del consiglio scientifico della Fondazione Symbola; direttore della rivista Scienza&Società edita dal Centro Pristem dell'università Bocconi di Milano; condirettore del web journal Scienzainrete edito dal Gruppo 2003.

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- **Ferruccio Trifirò -** Direttore de *La Chimica e l'Industria*, professore emerito dell'Università di Bologna.

Plenary Lectures

Kohzo Ito

Graduate School of Frontier Sciences, The University of Tokyo

GEN PL01 – "*Slide-Ring Materials: Novel Tough Polymers for Automobile*"

Anthony J. Ryan

The Grantham Centre for Sustainable Futures and the Department of Chemistry, The University of Sheffield, United Kingdom

GEN PL02 – *"What does sustainable mean in the context of chemistry?"*

Robert Schlögl

Max Planck Institute for Chemical Energy Conversion, Mülheim a.d. Ruhr & Fritz-Haber-Institute of Max-Planck-Institute, Berlin

GEN PL03 – *"Circular Economy of Carbon"*

GEN PL01

Slide-Ring Materials: Novel Tough Polymers for Automobile

Kohzo Ito

Graduate School of Frontier Sciences, The University of Tokyo; kozho@k.u-tokyo.ac.jp

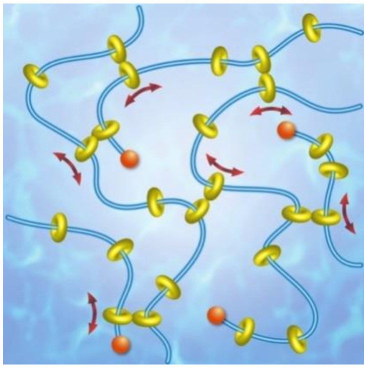

Fig.1. Schematic diagram of slide-ring materials.

We have recently developed a novel type of polymer network called *slide-ring materials* by cross-linking polyrotaxane, the supramolecular architecture with topological characteristics.1) In the network, polymer chains are topologically interlocked by figure-of-eight cross-links. Hence, these cross-links can pass along the polymer chains freely to equalize the tension of the threading polymer chains similarly to pulleys. The slide-ring gel or elastomer shows quite small Young's modulus, which is not proportional to the cross-linking density and much lower than those of chemical gels with the same density. This arises from the difference in the molecular mechanism of the entropic elasticity: While the conformational entropy is mainly responsible for the elasticity in usual chemical gels or rubbers, the mechanical properties of the slide-ring gel should be inherently governed by the alignment entropy of free cyclic molecules in polyrotaxane as well as the conformational entropy of backbone polymer. This means that the softness in the slide-ring gel is due to the novel entropic elasticity, which is also expected to yield sliding state and sliding transition. Consequently, the slide-ring materials have the dynamic coupling between two kinds of entropy: the conformational entropy of strings and alignment entropy of rings. 2,3) The concept of the slide-ring gel is not limited to cross-linked gels but also includes elastomer, cross-linked polymeric materials without solvent.

Accordingly it can be applied to wide area such as soft contact lens, paints, rubbers, soft actuator and so on. As a typical example, the scratch-resist properties of the self-restoring slide-ring elastomer were adopted into the top coating on the mobile phone.4) Finally, I would like to introduce ImPACT (Impulsing Paradigm Change through Disruptive Technologies) program, which is promoting to create flexible and tough polymers by using the slide-ring materials as a key technology.

In addition, we have recently developed mass-producing, low-cost, and free-standing nanosheets using topological self-assembly of cyclodextrins (CDs) and amphiphilic block copolymer, namely, pseudo-polyrotaxane (PPR) nanosheet by hierarchically ordered supramolecular self-assembly as shown Fig. 2.5) The PPR nanosheets were obtained by just mixing triblock copolymer and β-CD in water. β-CDs threaded on poly(propylene glycol) segment of the triblock copolymer to form a monoclinic single crystal with a dimension of 10-20 nm thickness and a few micro meters size. The PPR nanosheet can be applied to a novel drag delivery system with cell adhesiveness.

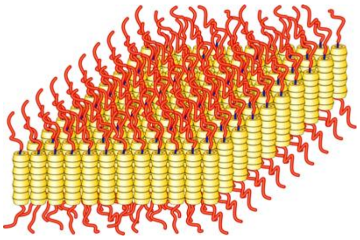

Fig.2. Schematic diagram of pseudo-polyrotaxane nanosheet.

References: 1. Y. Okumura and K. Ito, Adv. Mater., **2001**, 13, 485. 2. K. Kato and K. Ito, Soft Matter, **2011**, 7, 8737. 3. K. Mayumi and K. Ito, Soft Matter, **2012**, 8, 8179. 4. Y. Noda et al., J. App. Polym. Sci., **2014**, 131**,** 40509. 5. S. Uenuma et al., Chem. Commun., **2019**, in press.

GEN PL02

What does sustainable mean in the context of chemistry?

Anthony J Ryan

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The United Nations defines sustainability as “meeting the needs of the present without compromising the ability of future generations to meet their needs.” IUPAC has a more recent definition of Green Chemistry “the invention, design and application of chemical products and processes to reduce or eliminate the use and the production of harmful substances,” and sees it as a basic element of the UNs’ recent Sustainable Development Goals, in particular SDG 9 “Build resilient infrastructure, promote inclusive & sustainable industrialization, and foster innovation” and SDG 12 “Ensure sustainable consumption and production patterns”.

The 2016 COP21 Paris Agreement (United Nations Framework Convention on Climate Change (UNFCCC) dealing with greenhouse gas emissions, mitigation and adaptation) commits us to reducing our carbon emissions across a whole range of technologies. Chemistry as a whole needs to facilitate the transition from fossil-based energy and feedstocks to renewable energy and feedstocks that are fundamentally based on the use of sunshine in real-time (solar and wind) and in particular to develop scalable means to store that energy.

Polymer production accounts for < 3% of crude-oil consumption and < 1% of the global energy budget and overall has a beneficial (i.e. net negative) effect on global emissions due to light-weight vehicles reducing energy consumption, thermal insulation reducing the need for heating/air-conditioning and sensible food packaging reducing food waste, to give but three examples. Polymers have an important role to play in energy capture (photo-voltaics and wind turbines) and storage (batteries and water splitting). So what we need to do straight away is stop burning the fossil resource and maximize its beneficial use – in making plastics and other petrochemicals.

Life cycle analysis shows that an “eco-bag” made from hessian has to be used 140 times to be less energy intensive per use than taking a new PE bag each time, and if you reuse the PE bag then the effect is compounded. Yet self-identifying green consumers prefer hessian and paper to “nasty” plastics even when the evidence tells them otherwise. Does polymer science suffer from the same problem in the current emphasis on “sustainable”, i.e. renewable, polymers? The feedstocks for sustainable polymers *could* come from renewable resources, but their production should use less water and energy than the petrochemicals they replace. Currently, commercial “sustainable polymers” are made from plant starch or oils, or more preferably from agricultural waste streams that do not compete with food production. But why use a renewable feedstock to make a plastic if it results in much greater GHG emissions because of all of the processes involved?

This lecture will conclude by looking at how crystallization of polyolefins can be manipulated to get the most in terms of their properties. How the most abundant source of biomass (cellulose) could be modified to make engineering materials processed from water. How polymer photovoltaics can produce far more energy from the sun than was need to manufacture them. And how polyurethane foam and polythene films can combine with solar desalination to make deserts fertile and take CO_2 out of the atmosphere by using photosynthesis to grow food.

There is enough fossilized carbon to enable all these technologies and more. As long as we stop burning it! And this is the issue chemists should unite behind.

GEN PL03

Circular Economy of Carbon

Robert Schlögl

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Fossil energy carriers based upon carbon are used globally by means of a perfected technology chain for extraction, purification, transportation and storage. On this basis a global energy supply is organized. Defossilization replaces this technology chain by renewable but intermittent electricity. It cannot be stored, transported only in moderate amounts over medium distances and cannot replace applications where molecular energy carriers are essential (heavy duty applications, chemistry). It is thus desirable to augment the electrical renewable energy supply with a molecular renewable energy carrier that makes green electricity to a global commodity and solves the storage issue. Only then, a full functional energy system seems possible that is fully defossilized and globally operational.

The central molecular energy carrier accessible from renewable electricity is hydrogen. Its direct use is limited at acceptable system complexity. Reaction with carbon or nitrogen leads to carriers with usage profiles similar to their fossil counterparts and suitable energy densities for all applications. Recycling CO_2 from point sources or via technical or biological processes from the atmosphere closes the carbon cycle exactly in the same way as nature uses a carbon cycle between CO_2 and carbohydrates. The enormous advantages of bulk chemical energy conversion that can also supply the chemical industry with their raw materials post the oil age are counterweighted by substantial energy losses through the change of the carbon atom oxidation state (-4 in storage and +4 in used form) and the associated water formation plus the process inefficiencies of waters splitting and CO_2 reduction. These losses are then acceptable if dedicated solar energy primary converters are used in areas of the globe where renewable primary energy is available in large excess to local use. The fossil energy transportation system can continue its service for the transport of “green” energy and for the transportation of collected CO_2.

The use of such green molecular energy carriers in mobility applications (as “Diesel-electric hybrid”) does not close the carbon economy as the CO_2 emission remains diffuse. The defossilization benefit is consequently halved. This “carbon leak” is for some time tolerable with respect to the rapidly achievable savings in the total energy system by defossilization through a carbon cycle. Extended collection of atmospheric CO_2 can finally also remove this deficit and completely close the cycle.

The systemic cooperation of local green electricity with commodity synthetic carbon-based energy storage molecules allows for rapid transition into sustainable energy supply with a minimum of non-technical resistances and a maximum of retention of technology paths already existing. Basis is the insight that renewable primary electricity is the cheapest and inexhaustible energy source on the planet that can be harvested with a minimum of interference with the planetary spheres. Its cost is given by the energy harvesting and chemical energy conversion processes only, as transportation, storage and use systems are already existing and can be continued to be used. Overall system efficiency rather than process efficiency should thus govern decisions on roadmaps of energy transitions.

Poster and Brokerage Session

- **BE IL01 -** Luigi Nicolais, Caterina Meglio, Maria Emilia Mercurio, Aniello Cammarano *“Materias: a model for developing innovative science-based technologies”*
- **BE PO01** - Siglinda Perathoner (on behalf of the A-LEAF Consortium) *“An Artificial Leaf: a photo-electro-catalytic cell from earth-abundant materials for sustainable solar production of CO2-based chemicals and fuels (A-LEAF project)”*
- **BE PO02** - Ana Villacampa del Tiempo; Emma Palo; Carmen Claver; Fausto Gallucci; Blaž Likozar; Trond Halvorsen, Barbara Tišler; Olivier Vallet *“BIZEOLCAT: Bifunctional "Zeolite based Catalysts and Innovative process for Sustainable Hydrocarbon Transformation”*
- **BE PO03** - Gabriele Centi on behalf of ENERGY-X Steering Committee *“ENERGY-X: Transformative chemistry for a sustainable energy future”*
- **BE PO04** - Laura Cipolla “*Material design for regenerative medicine application: expertise and results”*
- **BE PO05** - Pier Luigi Gentili *“Soft Robotics and the Chemical Artificial Intelligence”*
- **BE PO06** - M. Grimaldi, A. Cavazza, C. Corradini *“Innovative material from agro alimentary by-products to realize a spray active packaging in a context of sustainability and Circular Economy”*
- **BE PO07** - Ester Colarusso, Maria Giovanna Chini, Stefania Terracciano, Ines Bruno, Simone Di Micco, Marianna Potenza, Simona De Vita, Patrizia Gazzerro, Assunta Giordano, Raffaele Riccio, Anil Bhushan, Panagis Filippakopoulos, Alfonso Reginelli, Giuseppe Bifulco, Gianluigi Lauro *“Identification of novel anti-leukemia agents targeting the bromodomain of BRD9”*
- **BE PO08** - Simona De Vita, Maria Giovanna Chini, Gianluigi Lauro, Marianna Potenza, Dafne Ruggiero, Stefania Terracciano, Ines Bruno, Raffaele Riccio, Jeffrey W. Bode, Andreas Koeberle, Oliver Werz, Francesco Maione, Alfonso Reginelli, Giuseppe Bifulco *“Inhibition of mPGES-1 and modulation of PGE2 biological activity for the treatment of colon cancer”*
- **BE PO09** - Gabriele Centi (project coordinator on behalf of the TERRA Consortium) *“TERRA: Tandem Electrocatalytic Reactor for Energy Resource Efficiency and Process Intensification”*
- **BE PO10** - Siglinda Perathonera (project coordinator on behalf of the OCEAN Consortium) *“OCEAN: New electrochemical solutions for industrial processing, which contribute to a reduction of carbon dioxide emissions”*
- **BE PO11** - Simone Maranghi, Maria Laura Parisi, Riccardo Basosi, Adalgisa Sinicropi *“Methodologies for the sustainability evaluation of novel chemical products for innovative renewable energy technologies”*
- **BE PO12** - Gabriele Centi on behalf of the Consortium *“SCOPE: An ERC Synergy Grant on Surface-COnfined fast-modulated Plasma for process and Energy intensification in small molecules conversion”*
- **BE PO13** - Roberta Ragni, Gabriella Buscemi, Danilo Vona, Marco Lo Presti, Gabriella Leone, Eleni Stavrinidou, Massimo Trotta, Gianluca Maria Farinola *“Hybrid Electronics based on Photosynthetic Organisms”*
- **BE PO14 -** Luca Antoniotti, Gustavo Capannelli, Antonio Comite, Anna Jezowska, Giancarlo Dondo, Simone Stasi, Sara Cepolina *“Pretreatment of waste lignocellulosic biomasses aimed at their chemical valorization”*

BE IL01

Materias: a model for developing innovative science-based technologies

Luigi Nicolais[a], *Caterina Meglio*[a], *Maria Emilia Mercurio*[a], *Aniello Cammarano*[a]

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The level of Innovation and Competitiveness of Italian research is at the top of world rankings. In fact, the analysis of the performance of world-wide research shows that the scientific productivity of Italian researchers is excellent: 3.5 articles published for every million dollars invested in research and development, thus recording levels of productivity and rates of growth very similar to Canada and second only to the United Kingdom (1). Moreover, Italy is a world leader in scientific production by number of citations in the Life Science sector (2).

However, analyzing the industrial impact of Italian scientific research, we realize that the transfer of research results is not among the best. This handicap derives from a weakness, of a quantitative and non-qualitative nature, which resides in the low investments in technology transfer activities and the lack of risk capital investments. In fact, venture capital intervention can support research in sectors with high potential contributing to the country's economy: the investment of venture capital in innovative start-up equity securities promotes high-skilled job opportunities for young people and raises the level of industrial development. The risks incurred by VC investors are high, especially for deep-tech innovations, i.e. with a high scientific and technological impact, as they require higher capital, longer lead times and uncertain returns compared to digital technologies.

In this context, Materias s.r.l. was born, in 2016, as a tool to support the technology transfer offices to allow the most promising technologies to overcome the so called "valley of death", through the connection of the research world with that of industrial companies, the development of innovative solutions in the field of advanced materials and the creation of new science-based businesses.

The work carried out by Materias in the first 3 years, has allowed the scouting of over 800 science-based ideas and technologies related to the field of advanced materials, ranging from life-science, cultural heritage, civil engineering to food-tech, from healthcare to transport.

In the initial phase of the project, Materias was engaged in a series of activities aimed at developing, protecting and enhancing its business model that allowed the company to increase its value and strengthen its intangible heritage by creating the database of technologies, first asset of the company. In particular, Materias model has been developed to support, in a very early stage of technologies, inventors and investors in choosing which project has the potential to be successfully transferred to the market. Moreover, one of the best innovation strategies of Materias is the opportunity to introduce new technologies into products by cross-fertilizing researches and scientific results. This approach is based on specific competencies (scientific and entrepreneurial) of Materias' team and of the International Industrial and Advisory Board. This approach is also a direct consequence of the ambition of Materias to constitute a bridge that connects research and industry. As explained in the Economic Assessment below, in order to achieve the realization of such an ambition, Materias decided to identify its three-fold activity (Scouting, InComing, Acceleration).

The Scouting activity aims to identify and evaluate innovative ideas generated by the academic sector and the research world. The ideas scouted are input in the Database. Once performed scouting, the idea is submitted to industrials.

The InCoMing (Incubation, coworking and merging) activity addresses idea development through technical-scientific assessments, technology validations, patent analysis, knowledge integration and cross fertilization. Through such operations, ideas mature and get ready to be accelerated. The objective is to accrete the value of ideas before their entry into the Market.

The Acceleration activity addresses the creation of market-ready solutions through the development of the business model and the prototype validation for the ideas incubated. Materias will evaluate the possibility to transform a market-ready solution in a Special Purpose Vehicle (SPV) by seeding it.

Thus, at the end of the acceleration process, either innovative business solutions are created and are ready to be invested into by Industrial or Institutional Investors, or IP value is enhanced and the idea, now adequately protected and structured, is ready to go on the market. In this activity Materias has invested only in 2% of technologies.

This modus operandi allowed Materias to create an ecosystem of Innovation with excellent Public and Private Research facilities, both national and international. This ecosystem not only created value in terms of networking, but also enabled Materias to make a decisive contribution to the development of technologies, becoming an active part in the process of technology transfer and early industrialization in collaboration with Universities and Institutions of Public Research, through the definition of a strategy aimed at overcoming the "valley of death".

And this scientific contribution and a prior art study, provided with the same “language” of scientists, allowed Materias to create some technological platforms and at the same time to file, as owner or co-owner and co-inventor, 23 Patents applications of which 13 are international. Materias' patent portfolio is also completed with the exclusive exploitation of the intellectual property of 3 international patents. Intellectual property, as well as providing a competitive advantage for the use of specific technologies, constitutes, through the offer of licenses or royalties to the industrial customer, one of the revenue streams on which the Materias business model is based.

In the last months the business model has been validated by two results: IP licensing of microneedles technology for transdermal delivery of active molecules to IBSA Institute Biochimique SA, a big Swiss pharmaceutical company, and the constitution of an innovative start-up focused on 3D printing of reinforced concrete with the support of Heidelberg Cement.

Reference 1: UK’s Department for Business, Energy & Industrial Strategy, 2016; Reference 2: The European House Ambrosetti, scimago data 2018.

BE PO01

An Artificial Leaf: a photo-electro-catalytic cell from earth-abundant materials for sustainable solar production of CO_2-based chemicals and fuels (A-LEAF project)

Siglinda Perathoner[a] *(on behalf of the A-LEAF Consortium)*

Consorzio INSTM – UdR Messina - CASPE Laboratory - C7o Dept. ChiBioFarAm, v.le F. Stagno D'Alcontres 31, 98166 Messina (Italy). perathon@unime.it

Mimicking the photosynthetic function of green plants and algae is one of the major technological challenges scientist around the world are facing nowadays. Natural photosynthesis transforms water (H_2O) and carbon dioxide (CO_2) into oxygen and carbohydrates using exclusively the energy of the sun. An artificial photosynthesis scheme will work in an analogous way, absorbing sunlight to combine water and CO_2 into oxygen and chemicals, including fuels.

A-LEAF European consortium seeks the realization of an artificial photosynthesis platform: for the capture and transformation of solar energy into chemical energy, as sustainable substitute for fossil resources. A-LEAF starts from atomic-scale studies to determine experimentally and theoretically the main parameters for optimization of the chemical transformations at surfaces to combine water and CO_2 into oxygen and energy-rich chemicals. This knowledge will be transferred and up-scaled into (photo)electrochemical set-ups to maximize performance. The champion components will be combined into a single photoelectrocatalytic (PEC) device: an artificial leaf. This multidisciplinary and comprehensive project will be executed by young and renowned European researchers from 13 recognized institutions located in 8 European countries, including COVESTRO, a world-wide leading materials company.

Beyond the scientific challenge, A-LEAF also commits to a low-cost approach. Solar fuels will only have societal impact if they can compete with fossil fuels in the marketplace. A-LEAF is working with competitive materials and processes, avoiding the use of precious metals, or rare/expensive raw materials. A minimum price point is the objective, as ambitious and relevant as efficiency or reliability. The dream is to obtain economic sustainable fuels and chemicals. Fuels from sunlight, water and atmospheric CO_2. Exclusively using carbon, silicon, iron, or copper. A-LEAF is working hard to make this dream come true.

A-LEAF is also featured as a 'Success Story' in the European Commission webpage: 'Solar fuels turns to plants for inspiration' and in a piece of news of Digital Single Market 'Using the energy from the sun to get fuels'

OCEAN is a FETPROACT-2016 projects. Grant agreement ID: 732840. The project is coordinated by Prof. José Ramón Galán-Mascarós from the Institute of Chemical Research of Catalonia, Spain. (ICIQ). Project started on Jan 1st, 2017 and is about at half of his planned activities.

For contacts, news and further information, visit the project web site: http://www.a-leaf.eu/project/.

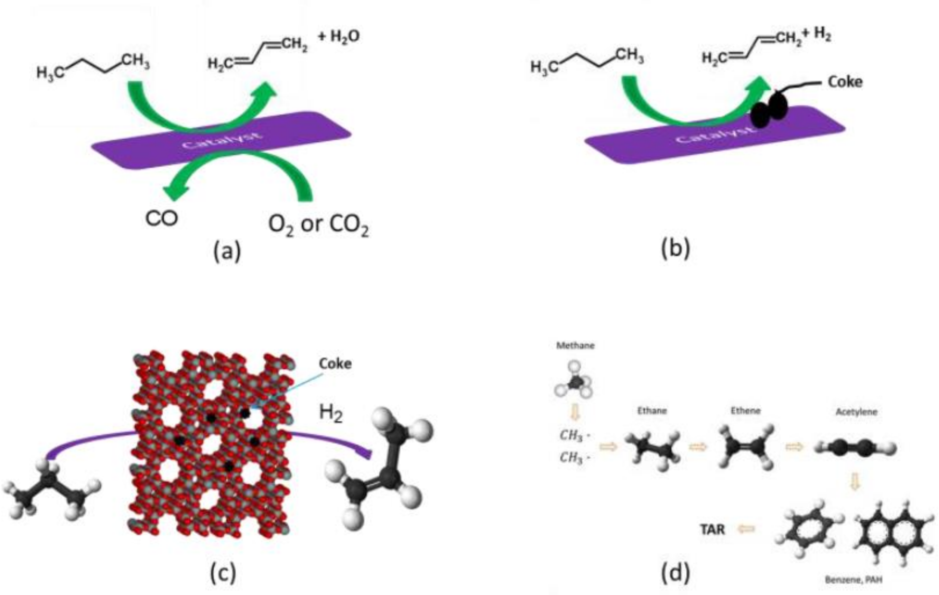
BE PO02

BIZEOLCAT: Bifunctional Zeolite based Catalysts and Innovative process for Sustainable Hydrocarbon Transformation

Ana Villacampa del Tiempo [a]*; Emma Palo* [b]*; Carmen Claver* [a]*; Fausto Gallucci* [c]*; Blaž Likozar* [d]*;*
Trond Halvorsen [e]*, Barbara Tišler* [d]*; Olivier Vallet* [f]

[a] *Fundaciò Eurecat – Barcelona (Spain),* [b] *NextChem – Rome (Italy);* [c] *Eindhoven University of Technology – Eindhoven (The Netherlands);* [d] *National institute of Chemistry - Lubljana (Slovenia);* [e] *Sintef AS – Oslo (Norway);* [f] *Strane Innovation SAS - Gif sur Yvette (France)*

In the past there have been a number of semi-industrial trials and even commercial processes to obtain on-purpose petrochemical feedstocks from methane and/or propane (more generally, C1-C4 hydrocarbons). However, their commercial success has been limited due to several reasons: from technical drawbacks (low conversions and selectivity) to economics (high capital investment and high operation costs are often obtained). Furthermore there is a need for lowering the carbon footprint of gas and oil industry, i.e. refining industry, contributing to an evolving scenario of sustainable economy in such field. BIZEOLCAT is addressing the use of light alkanes as raw material for specialty chemical industry and not as feedstock for fuels in the current oil refining process, becoming part of this transition. BIZEOLCAT will aim developing 4 new processes of light alkanes (methane, propane and butane) conversion to olefins (propylene, butadiene) and to aromatics demonstrating higher performance, cost efficiency and environmental sustainability, using innovative methodologies for catalysts preparation and membrane reactor design. A refining company, TUPRAS, will run the pilot unit experiments. Two large companies, CEPSA and PERSTORP, will validate propylene and propylene and benzene, respectively as part of TR5 validation. sLCA have demonstrated that the expected reduction in the greenhouse emissions related to the manufacturing of propane dehydrogenation developed within the project and also the Aromatization process



Four new approaches using advanced catalysts addressed in BIZEOLCAT a) oxidative BDH and b) non oxidative BDH c) PDH and d) Aromatization of methane with improved reactor technologies.

BE PO03

ENERGY-X: Transformative chemistry for a sustainable energy future

Gabriele Centi[a] on behalf of ENERGY-X Steering Committee

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ENERGY-X .is an EU-funded CSA project aiming at building a strategic roadmap towards a large-scale research initiative addressing the efficient conversion of solar and wind energy into chemical form. It includes 13 core partners across Europe: i) Technical University of Denmark, ii) Max Planck Society, iii) Ghent University, iv) Polish Academy of Sciences, v) CEA, vi) Czech Academy of Sciences, vii) Utrecht University, viii) ERIC aisbl, ix) ETH Zürich, x) RWI, xi) Technical University of Valencia, xii) DECHEMA, and xiii) EERA aisbl, and is supported by a large group of industrial companies.

CHALLENGE: ENERGY-X will address one of the grandest challenges of modern society: how can we give a growing number of people on Earth the required energy and materials, and can we do this in such a way that we reduce our environmental footprint and abate climate change? ENERGY-X addresses the essential missing component (X) in the future European energy and chemical production landscape: technologies to replace fossil resources.

VISION: ENERGY-X will provide the disruptive new science and technology enabling efficient conversion of solar energy into chemical form and will combine this ambition with scale-up to industrially relevant scale by integrating with European industry. To enable efficient energy conversion we need discovery of new catalysts as well as novel integrated conversion approaches. The enabling science is molecular and interfacial catalysis.

DEMONSTRATION: ENERGY-X will not only create scalable scientific solutions but also transfer this knowledge into two demonstrator projects, namely, the manufacturing of carbon- neutral aviation fuels and the decentralized production of fertilizers with no CO_2 footprint.

For contacts, news and further information: contact@energy-x.eu and the project web site: www.energy-x.eu..

BE PO04

Material design for regenerative medicine application: expertise and results

Laura Cipolla

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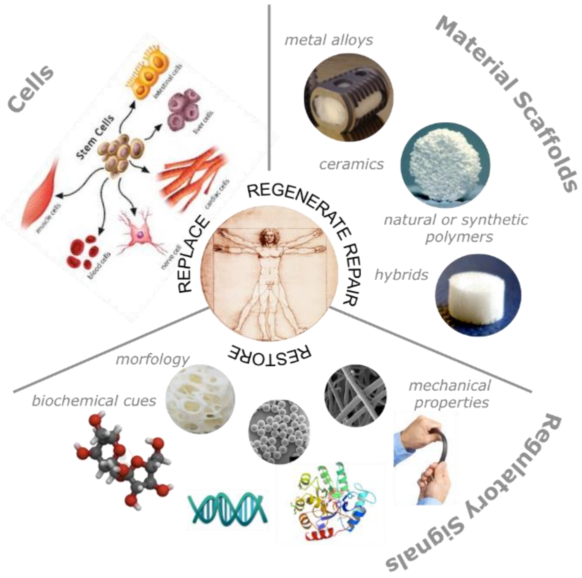
In the field of material design for regenerative medicine, there is a need to better understand and control the biological responses, and for tools that can drive cell fate towards tissue repair and regeneration. In addition to biochemical signals, material chemistry is at the basis for tuning mechanical properties of the materials.



In the last few years my research has been focussed on biomaterial bioactivation through different strategies, including chemical grafting of bioactive molecules such as peptides and carbohydrates, as well as sol-gel formulation in order to tune organic-inorganic hybrid materials mechanical properties. The expertise deals with different materials, ranging from inorganic ones such as hydroxyapatites for bone tissue engineering, to fully synthetic organic-inorganic hybrids for cartilage regenerative approaches (1) and natural biopolymers. i.e. collagen and gelatin 2D or 3D scaffolds for neuronal regeneration (2).

Different results and projects will be briefly outlined.

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BE PO05

Soft Robotics and the Chemical Artificial Intelligence

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The technological development of our societies is guided by the will of helping humans in manual and mental labor. With the advent of the industrial revolution, which began in the eighteenth century, many machines performing heavy manual labor have been devised, thus leading to a noticeable economic and social progress. Since the early 1950s, electronic computers instructed by software have been contrived to perform numerical computations and relieve humans from mental labor. A long-cherished aspiration is to design machines that can help humans in both manual and mental activities, at the same time. Such machines, called robots, are programmable and potentially able to carry out many actions peculiar to humans. In fact, robots are usually able to perceive signals through sensors, plan actions through internal cognitive processes, and act through actuators, as the human nervous system does through its sensory cells, brain, and effector system made of muscles and glands. Traditionally, robots are made of electronic circuits, computer software, mechanical rigid parts, and electric motors, and are designed especially for accomplishing dangerous tasks, such as bombs disposal, deep ocean, and planetary exploration. Recently, the idea of developing robots grounded on wetware rather than on hardware is taking shape (1-3). A "Soft Robot", also called "Chemical Robot", is thought as a molecular assembly that reacts autonomously to its environment through molecular sensors, makes decisions by its intrinsic artificial neural networks, and performs actions upon its environment through molecular effectors. Chemical Robots should be easily miniaturized and implanted in living beings to interplay with cells or organelles for biomedical applications. Chemical Robots should become auxiliary elements of the immune system.

In our group, we are devising sensory modules (4), artificial neuronal networks (5), and effector modules (6) by using molecular, supramolecular, and systems chemistry. To develop our modules, we pursue a methodology that requires an analysis of the human nervous system at three levels: at the computational, algorithmic, and implementation levels. We find that a good model of the human ability to compute with words is Fuzzy logic. Therefore, we are proposing innovative methods to process Fuzzy logic by using molecules, supra-molecules, and chemical systems far-from-equilibrium (7). We are tracing a new path in the field of Artificial Intelligence, because we are mimicking some performances of the human intelligence in "wetware", i.e., solutions of peculiar chemical systems (8).

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BE PO06

Innovative material from agro alimentary by-products to realize a spray active packaging in a context of sustainability and Circular Economy

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In the late years, the European Community directives are focusing on an ambitious plan promoting the idea of Circular Economy (1), aimed at waste reduction and enhancing of recycling processes. The main goal of this innovative trend is to move towards environmental sustainability. An interesting example to support the strategy of "closing the loop" is represented by the use of by-products from agro-industrial field that can be inserted in the productive cycles as new resources. High amounts of vegetables are in fact not suitable for commercial use, and large portions of plants are normally discarded. Such by-products are still rich of valuable molecules characterized by bioactive properties, antioxidant and antibacterial (2,3), therefore their use to obtain in new products could provide an additional economic value.

The aim of this study is to use the extracts from this material to realize a new biopolymer characterized by biodegradability and compostability, and that can be used as starting point to obtain an innovative, active and edible packaging.

Experiments to realize the polymer have been made by preparing extracts of by-products derived from onions, artichokes, asparagus, cardoons and grapes, and adding them to selected ingredients, leading to a solution that can be sprayed on food products. The solution, once dried, forms a thin and transparent coating having antioxidant and antibacterial properties, and acts as active packaging that protects the products and enhances their shelf-life. The polymer can be enriched with several active molecules, including flavours, prebiotics and nutraceuticals, tailored for each type of food. The film application has been tested on several products such as meat, fruits and vegetables, and showed a great efficacy in prolonging their shelf-life (4).

Furthermore, this innovative material can represent a good solution to realize several new technologies, according to the new European Directive that banned the single-use plastics by 2021. For example, when sprayed on paper and cellulosic packaging, this product has the effect of realising a coating impermeable to oils and fats, thus permitting the use of paper to replace multilayer materials based on plastics.

This poster is also presented as WS5 PO22

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BE PO07

Identification of novel anti-leukemia agents targeting the bromodomain of BRD9

Ester Colarusso[a]*, Maria Giovanna Chini*[a]*, Stefania Terracciano*[a]*, Ines Bruno*[a]*, Simone Di Micco*[a]*, Marianna Potenza*[a]*, Simona De Vita*[a]*, Patrizia Gazzerro*[a]*, Assunta Giordano*[a]*, Raffaele Riccio*[a]*, Anil Bhushan*[b]*, Panagis Filippakopoulos*[c]*, Alfonso Reginelli*[d]*, Giuseppe Bifulco*[a]*, Gianluigi Lauro*[a]*.*

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Introduction: Bromodomains are druggable protein modules able to recognize post-translational modifications (PTMs) on histones and involved in diverse diseases. Among them, bromodomain-containing protein 9 (BRD9), a subunit of the mammalian SWI/SNF chromatin remodeling complex, has emerged as a key-factor for a series of disorders. Recent studies have revealed the key role of SWI/SNF in leukemia (1) and BRD9, as part of this complex, suppresses the proliferation of mouse and human acute myeloid leukemia (AML) cell lines when its bromodomain is inhibited by a small molecule.

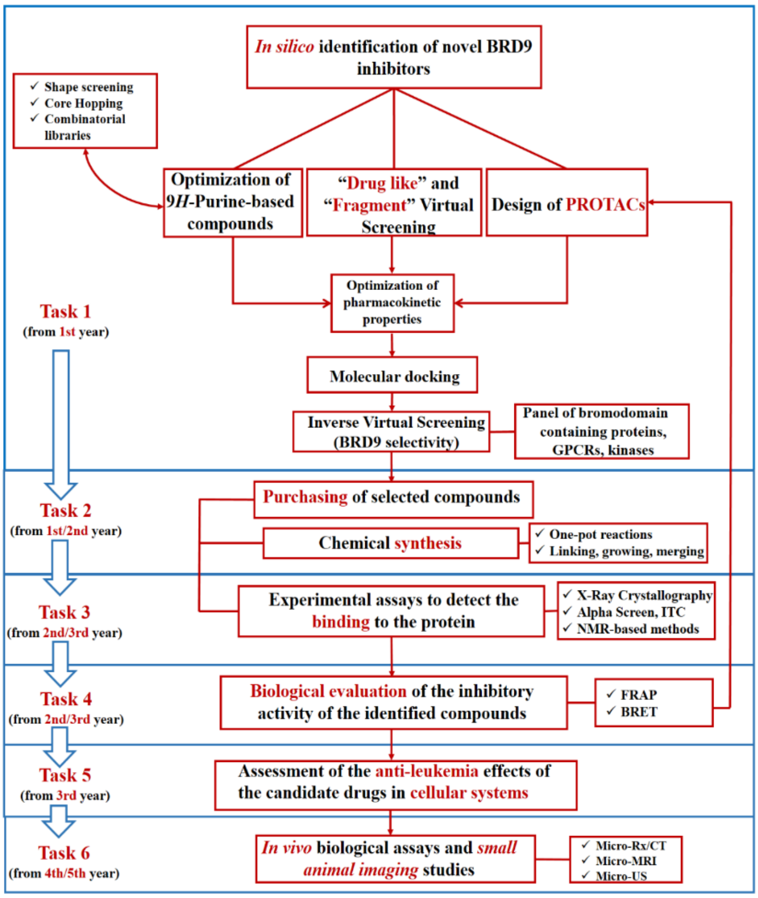

Figure 1. *Experimental workflow for the discovery of new BRD9 inhibitors (3)*

Aims: Thanks to the support provided by the Fondazione AIRC per la Ricerca sul Cancro (2), the discovery of novel compounds targeting BRD9, focusing on their use as anti-leukemia drugs, represents the main aim of this project.

Experimental plan: New, potent, and selective inhibitors of BRD9 protein will be identified applying a multidisciplinary approach following a well-structured workflow (Figure 1). Specifically, three main paths will be followed: the already available 9*H*-Purine scaffold (previously discovered in our research group) (3) will be optimized, "Fragment" and "Drug-like" Virtual Screening will be carried out to identify now promising scaffolds, and new Proteolysis targeting chimeric molecules" (PROTACs) will be designed. The identified inhibitors will be selected to perform specific binding assays and *in vitro* biological assays with the aim of developing promising anti-leukemia/anticancer drugs and to further corroborate the biological role of BRD9 in these diseases. Afterwards, compounds determining a cellular response in acute myeloid leukemia (AML) cell lines will then represent the starting point for future investigations aimed to develop further potent and selective molecules active in AML animal models.

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BE PO08

Inhibition of mPGES-1 and modulation of PGE_2 biological activity for the treatment of colon cancer

Simona De Vita[a], *Maria Giovanna Chini*[a], *Gianluigi Lauro*[a], *Marianna Potenza*[a], *Dafne Ruggiero*[a], *Stefania Terracciano*[a], *Ines Bruno*[a], *Raffaele Riccio*[a], *Jeffrey W. Bode*[b], *Andreas Koeberle*[c], *Oliver Werz*[c], *Francesco Maione*[d], *Alfonso Reginelli*[e], *Giuseppe Bifulco*[a].

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Background: Prostaglandin E_2 (PGE_2) represents the most important bioactive lipid in the human body able to regulate physiological and pathological events, such as inflammation and cancer. PGE_2 is produced by microsomal prostaglandin E_2 synthase (mPGES) from PGH_2, and the inducible isoform mPGES-1 is responsible for PGE_2 level elevation detected in cancer events. The specific biological functions of PGE_2 arise from the signalling pathways after binding to specific EP receptors. The relationship between mPGES-1 expression, PGE_2 levels, and colon/colorectal cancer (CRC) has been proven. In preclinical models of various types of cancer, the chemo-resistance to specific anticancer agents has been strongly reduced when the activity of PGE_2 is suppressed.
Aims: The main aim of this project is the development of new mPGES-1 inhibitors/EP antagonists against CRC. Thanks to the support provided by the AIRC foundation (1), a large set of identified compounds able to inhibit mPGES-1 *in vitro* will be evaluated to assess their anti-inflammatory/anticancer activities *in vivo*. Also, the biological profile of a first small set of mPGES-1 inhibitors has been already preliminarily evaluated *in vivo* and by small-animal imaging (2), leading to promising results and then encouraging further investigations. The reduction of chemoresistance to cytotoxic agents (e.g. oxaliplatin) by inhibiting the activity of PGE_2 will be evaluated.
Experimental plan: The design of mPGES-1 inhibitors/EP antagonists will be performed *in silico* and then synthesized and/or purchased. After assessing the binding to the proteins of interest (mPGES-1, EPs), the biological inhibitory activities of the candidate drugs will be assessed *in vitro*. The chemo-resistance to selected anticancer drugs (e.g. oxaliplatin) will be investigated *in vitro* in the presence of the candidate drugs. The biological activity of the most promising compounds will be assessed *in vivo* also evaluating their toxicity. The reduced chemo-resistance in the presence of the candidate drugs will be then also assessed *in vivo*. The dynamic evaluation of anti-inflammatory/anti-cancer effects will be performed by multimodality small-animal imaging approach, and afterwards, *ex vivo* biochemical/histological analysis will be performed.

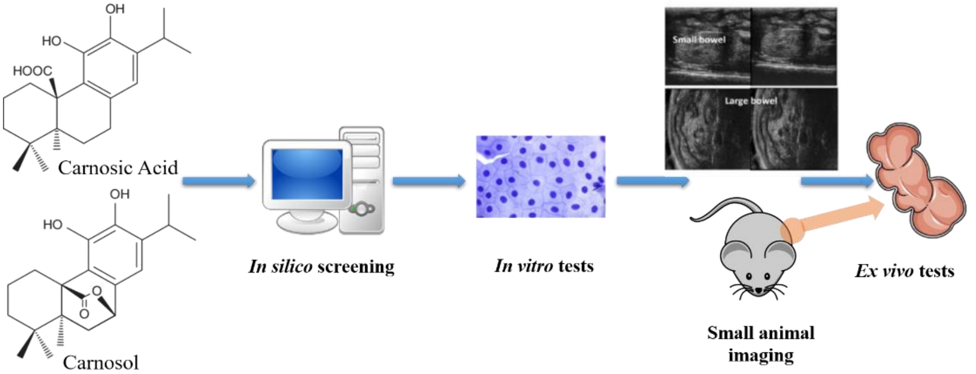

Figure 2. *Experimental plan for the discovery of new mPGES-1 inhibitors/EP agonists.*

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BE PO09

TERRA: Tandem Electrocatalytic Reactor for Energy Resource Efficiency and Process Intensification

Gabriele Centi[a] *(project coordinator on behalf of the TERRA Consortium)*

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TERRA aims to develop, from TRL 3 to 5, a tandem electrocatalytic reactor (TER) coupling an oxidation reaction to a reduction one, with thus the great potential advantage of

- saving resources and energy (needed to produce the oxidant and reductants for the two separate reactions);
- intensify the process (reduce the nr. of steps, coupling two synthesis processes and especially eliminating those to prepare the oxidation and reduction agents).

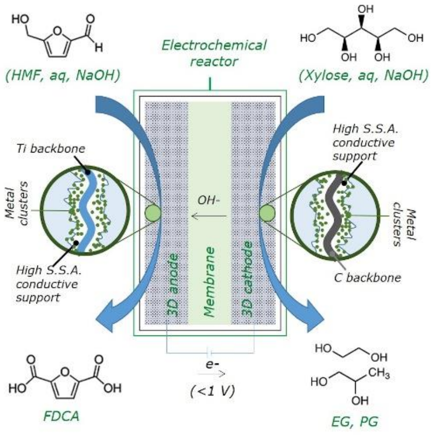
The TER unit may be used in a large field of applications, but will be developed for a specific relevant case: the synthesis of PEF (PolyEthylene Furanoate), a next generation plastic.

The TER unit may be used in a large field of applications, but will be developed for a specific relevant case: the synthesis of PEF (PolyEthylene Furanoate), a next generation plastic. TERRA project aims to make a step forward in this process by coupling the FDCA and MEG synthesis in a single novel TER reactor, with relevant process intensification. Between the elements of innovation of the approach are:

- operation at higher T,P than "conventional" electrochemical devices for chemical manufacturing;
- use of noble-metal-free electrocatalysts and novel 3D-type electrodes to increase productivity;
- use of electrode with modulation of activity;
- possibility to utilize external bias (from unused electrical renewable energy) to enhance flexibility of operations.

In addition to scale-up reactor and test under environmental relevant conditions (TRL 5), the approach in TERRA project is to address the critical elements to pass from lab-scale experimentation to industrial prototype with intensified productivity. These developments are critical for a wider use of electrochemical manufacturing in chemical and process industries.

TERRA is part of the SPIRE projects (https://www.spire2030.eu/projects/our-spire-projects), under the area process intensification. Grant agreement ID: 677471. The project is coordinated by European Research Institute of Catalysis A.I.S.B.L.



For contacts, news and further information, visit the project web site: http://www.terraproject.it

BE PO10

OCEAN: New electrochemical solutions for industrial processing, which contribute to a reduction of carbon dioxide emissions

Siglinda Perathoner[a] *(project coordinator on behalf of the OCEAN Consortium)*

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The OCEAN project aims to develop an integrated process for the production of high-value C2 chemicals from carbon dioxide using electrochemistry. This will be achieved by:

1) Improving and optimizing a TRL5 technology that can convert carbon dioxide to formate, to TRL6. OCEAN will bring this technology just one-step away from commercialization, by demonstrating this technology at the site of an industrial electricity provider, converting 250g of CO_2 per hour at 1.5 kA/m^2. The energy efficiency will be improved by coupling the cathodic reaction to the oxidation of sugars at the anode, using a novel technology to match the kinetics of the reactions at both electrodes. The obtained formate can be converted to oxalate.

2) Developing new electrochemical methodologies to further convert formate and oxalate to formic acid and oxalic acid, respectively. Novel salt-splitting will be investigated using bipolar membranes. Again, this allows for direct coupling with an electrosynthesis step at the anode and/or cathode.

3) Developing new electrochemical methodologies by converting oxalic acid to glycolic acid and other high-value C2-products, these will be benchmarked with conventional hydrogenation.

4) Integrating the TRL6 and new (TRL4-5) electrochemical technologies in an industrial process, aimed at the production of high-value C2 products and polymers thereof by developing the process steps needed to produce oxalate, C2 products and polymers.

5) Demonstrating the economic feasibility by performing a market analysis and making a business case and exploitation strategy.

OCEAN is part of the SPIRE projects (https://www.spire2030.eu/projects/our-spire-projects). Grant agreement ID: 767798. The project is coordinated by European Research Institute of Catalysis A.I.S.B.L.

For contacts, news and further information, visit the project web site: https://www.spire2030.eu/ocean..

BE PO11

Methodologies for the sustainability evaluation of novel chemical products for innovative renewable energy technologies

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The design and optimization of novel chemical products and processes for energy generation technologies should be always supported by sustainability assessment (1, 2). This is essential to provide a reliable appraisal of the environmental, economic and social burdens associated to a product or process, and reasonable market implications. Methodologies based on Life Cycle Thinking approach (i.e., Life Cycle Assessment, Life Cycle Costing, Social Life Cycle Assessment, Life Cycle Sustainability Assessment) are strategic tools to achieve this aim.

In particular, Life Cycle Assessment (LCA) is diffusely applied to perform an environmental assessment in this field (3). If used to its fullest potential, it allows a multi-level investigation of the system integrating resource and energy efficiency optimization, critical raw materials analysis and circular economy aspects (4). The LCA analytical approach permits an outlining of the environmental profile of a product or process system during its whole life cycle, from raw materials extraction to end-of-life phase.

In this work, we present the major outcomes resulting from the application of LCA to innovative chemical products for renewable energy production technologies. The analysis is performed for the calculation of the environmental footprint to highlight the hotspots of the system under study, focusing on the behavior of the novel chemical products employed in the investigated energy production technologies. In particular, we investigated the environmental burden and the more sustainable alternatives of some chemical compounds diffusely used in innovative photovoltaic technologies (4).

This poster is also presented as WS5 PO05

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BE PO12

SCOPE: An ERC Synergy Grant on Surface-COnfined fast-modulated Plasma for process and Energy intensification in small molecules conversion

Gabriele Centi on behalf of the Consortium

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SCOPE is an EU-funded ERC Synergy project (Project ID: 810182, Call: ERC-2018-SyG project, started on April 2019, 6th years) coordinated by Gabriele CENTI of the University of Messina (Italy) and involving the Universities of Antwerp (Annemie BOGAERTS, University of Antwerp, Belgium), Warwick (Evgeny REBROV, Volker HESSEL, UK), of Adelaide (Australia) and the Technische Univ. Eindhoven (The Netherlands). The project integrates complementary and interdisciplinary competences over the entire scale elements necessary for process development, from nano to mega scale, from catalysis and plasma level to plant sustainability and assessment

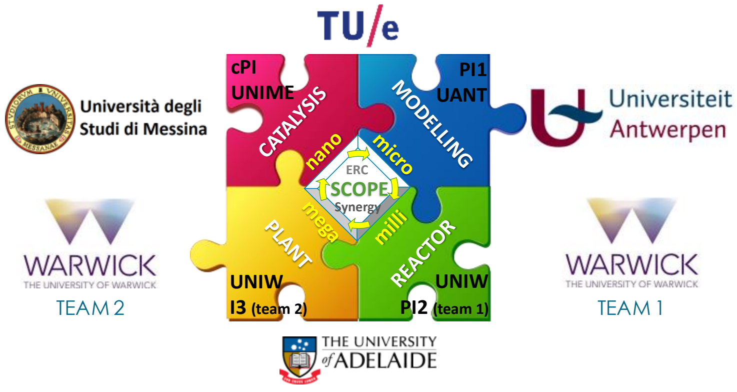
AMBITIOUS: We will develop the scientific bases for a ground-breaking approach (based on catalysis-plasma symbiosis) for direct chemical syntheses using renewable energy of large-volume key chemicals or energy vectors.

THE SCIENTIFIC ISSUE: Non-thermal plasma is a potential valuable technology for direct chemical syntheses with large reduction of carbon footprint (up to over 90%) (process and energy intensification), but selectivity and energy efficiency is an issue (<20-30%).

THE PROJECT IDEA: A highly innovative approach for non-thermal plasma symbiosis with catalysis. It is based on three brand new ideas to overcome the actual limits and enhance the selectivity (to valuable products) and energy efficiency (as exergy) to levels (>70-80%) suitable for exploitation.

THE TARGET REACTIONS:

1. *N_2 fixation.* key reaction for production of ammonia (NH_3) and NOx-made fertilizers, one of the largest volume chemicals (over 150 Mt/y production). Today, an energy-intensive multistep process is required, starting from CH_4 and air, via H_2 production, NH_3 synthesis and NH_3 oxidation to NOx.
2. *CH_4 valorization* to produce longer C-chain hydrocarbons, and especially ethylene and propylene, which are the building blocks of current petrochemistry (over 200 Mt/y production). Their current production from methane requires a multistep and energy-intensive process: syngas production, methanol synthesis and methanol-to-olefin conversion.
3. *CO_2 conversion to liquid solar fuels*, like methanol or higher alcohols. Key process to make chemical energy storage possible, a fundamental technology to allow the storage/distribution on long distance (world-scale) of renewable energy. Today several steps: H_2 production, syngas formation, methanol synthesis, further steps to arrive to higher alcohols.



BE PO13

Hybrid Electronics based on Photosynthetic Organisms

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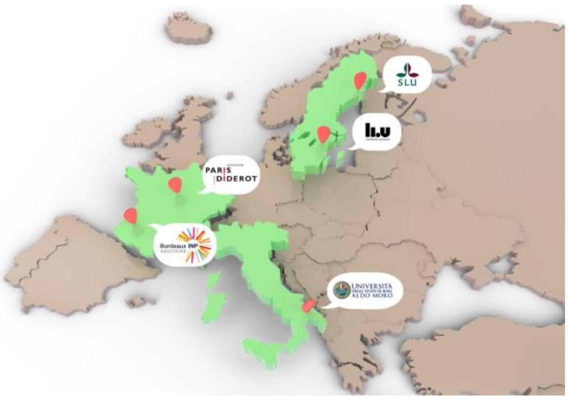
HyPhOE aims to establish a revolutionary symbiosis between photosynthetic organisms and technology, and to rethink and re-establish the concept of green technology. Photosynthetic organisms are intelligent, with unique functions and capabilities, being able to harvest solar energy, synthesize food, and sequester pollutants (1-). As the boundary between technology and Nature is fading, Nature is being used as part of the technology and technology is enhancing Nature. HyPhOE will be integrated in urban settings, agriculture, and forestry – transforming and elevating our interaction with green organisms tapping into the energy and biochemical cycles of the ecosystem.

The logo of the FET-Open Project HyPhOE

The ultimate goal of HyPhOE is to develop advanced bio-hybrid systems based on photosynthetic organisms and smart materials and devices. Our strategy relies on developing a set of tools and methods for bi-directional electronic and chemical interfacing with photosynthetic organisms that will comprise the backbone of the project and pave the way for the targeted applications: ***i***. Energy systems based on electronically-functionalized plants and photosynthetic organisms. ***ii***. Plant physiological control using bioelectronics systems. ***iii***. Environmental monitoring using functionalized plants.

We aim to take the concept of electronic-photosynthesis beyond proof-of-principle and to the next level of sophistication by electronic-smart functionalization of rooted plants and system integration.



Location of the teams participating to HyPhOE

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(3) Trotta M., Farinola G., et al. Angew. Chem. 2012, 51, 11019
(4) Simon D. T. et al. Chem. Rev., 116 (21), 13009–13041 (2016)
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BE PO14

Pretreatment of waste lignocellulosic biomasses aimed at their chemical valorization

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In the last few decades the concepts of sustainability and of circular economy grew in importance. The aim is to develop new processes able to minimize both the amount and the impact of the waste by reusing the greater part of products and byproducts (1). The present work has been carried out in the frame of the H2020 "FORCE – Cities Cooperating For Circular Economy" project which is rooted on such concepts and deals with innovative ways to reuse and exploit waste materials in four EU cities: Hamburg, Lisbon, Copenhagen and Genoa (2). The City of Genoa focuses on the subject matter of waste wood.

The goal was to develop a viable process able to transform different waste woods into higher value products through a double-step process (pretreatment and biotechnological treatment). The pretreatment step aims at reducing the recalcitrance of the lignocellulose fraction (3), while the treatment step ought to degrade the macromolecular structures composing it (cellulose, hemicellulose, lignin) into low molecular weight products (such as monosaccharides from cellulose and hemicellulose, various products including substituted phenols from lignin) (4).

Liquid Hot Water and *Steam Explosion* techniques were investigated as pretreatment step in different conditions (pressure, temperature, time, using both a commercial autoclave and a custom reactor. To handily compare different experiments, the Severity Factor (3,4) was used.

Morphological and structural changes were investigated by optical microscopy and field emission scanning electron microscopy (FESEM), whereas the surface area was determined by N_2 adsorption at 77 K. The biotechnological treatment was performed by Active Cells S.r.l. (Genoa) employing enzymes produced by *Trametes Versicolor*, *Penicillum spp*., *Trichoderma spp*. and *Aspergillus Niger*. Those fungi and molds were chosen according to their ability to produce cellulases, hemicellulases and lignin-modifying enzymes (3).

The aqueous solutions produced by the biotechnological treatment were characterized by means of Chemical Oxygen Demand (COD), total carbohydrates content through the phenol-sulfuric method (6) and total phenols content using the Folin-Ciocalteu method (7).

The pretreatment step has shown an increase in the surface area of the waste wood up to 15 times after moderate severity *Steam Explosion* pretreatment (log R_0 = 3,8-4,0) and the pretreated wood demonstrated itself a suitable substrate for the enzymatic hydrolysis. Currently, a sequential biotechnological treatment has shown to be the most promising, with a moderate conversion (typically 20%) but an interesting selectivity in fermentable sugars (>66%), higher than the previously attempted conversion routes.

This poster is also presented as WS2 PO16

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WS1 - CHEMISTRY FOR SECURE SOCIETY

The workshop will highlight the pervasive role of Chemistry in the field of security, in terms of detection, prevention, protection, mitigation and defence against the use of hazardous materials, highly toxic chemicals and dangerous products (e.g. explosives, poisons, bio-toxins, radioactive agents) for criminal purposes.

Following a trans-disciplinary approach, spanning from advanced analytical chemistry to materials science, from sensor technology to catalysis, the latest advances in the field of rapid detection, personal protection, decontamination and security policies will be presented and discussed by eminent experts from academia, research institutions, industry and governmental agencies, working on a daily basis for secure, resilient and ethically correct societies.

WS1 - Organizing Committee and Conveners

- Matteo Guidotti, CNR-ISTM, Milano
- Elisa Michelini, University of Bologna
- Vincenzo Vaiano, University of Salerno
- Ernesto Salzano, University of Bologna
- Domenica Tonelli, University of Bologna
- Stefano Econdi, CNR-ISTM, Milano

WS1 - Keynote Lectures

- **WS1 KN01** – Genserik Reniers, TU Delft, the Netherlands, *“Integrating safety and security measures to avoid chemistry-related domino effects”*.
- **WS1 KN02** – Adolfo Gregori, Carabinieri, Department of Scientific Investigation (RIS), Italy, *“Simultaneous Determination of Gunshot Residues and Stabilizers in Forensic Samples by means UHPLC-HRMS analysis”*.
- **WS1 KN03** – Arben Merkoçi, Inst. Català de Nanociencia i Nanotecnologia, Barcelona, Spain, *“Nanobiosensors for diagnostics: from health, environment to safety and security applications”*.
- **WS1 KN04** – Chiara Bisio, University of Eastern Piedmont, Alessandria, Italy, *“Innovative layered materials as active allies for the decontamination of toxic chemical agents”*.
- **WS1 KN05** – Vasile Parvulescu, University of Bucharest, Romania, *“Photocatalysis versus plasma-coupled catalysis for the mineralization of warfare and harmful compounds”*.
- **WS1 KN06** – Mauro Marchetti, CNR-ICB, Sassari, Italy, *“Hypothesis of remote identification of warfare chemical agents and explosives after blast of chemical bombs”*.
- **WS1 KN07** – Fabiana Arduini, University of Rome Tor Vergata, Italy, *"Early and on site detection of chemical and biological warfare agents using miniaturised electrochemical biosensors"*.
- **WS1 KN08 -** Sergey Zinoviev - OPCW, International Cooperation Officer, the Netherlands,*“Working for the Chemical Weapons Convention: interdisciplinary expertise and funding opportunities"*

WS1 KN01

Integrating safety and security measures to avoid chemistry-related domino effects

Genserik Reniers[a], *Chao Chen*[a]

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In this keynote presentation, first the difference is elaborated between accidental and induced large-scale knock-on related accidents or so-called domino effects. The research advances with respect to domino effects are expounded and it is obvious that security aspects represent the latest advances of this research field. Previously, domino effects have been studied from different perspectives: vulnerability and index analysis (with experiments, simulations, and determining thresholds), quantitative assessment (using for instance Probit models, Bayesian Networks, Petri-nets), and management modeling (for example using emergency planning for a multi-plant setting, using economic approaches or using game theoretic models). The presentation further elaborates on current research on the integration of safety and security resources to prevent domino effects. An approach is developed based on dynamic graphs and the modeling of the spatial-temporal evolution of such events, and economic optimization modeling.

WS1 KN02

Simultaneous Determination of Gunshot Residues and Stabilizers in Forensic Samples by means UHPLC-HRMS analysis

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[a]Sapienza University of Rome, Department of Chemistry, 00185 Rome, Italy; [b]University of Teramo, Faculty of Bioscience and Technology for Food, Agriculture and Environment, 64100; [c]Carabinieri, Department of Scientific Investigation (RIS), 00191 Rome, Italy; adolfo.gregori@carabinieri.it

In recent years, due to the increasing use of ammunition without lead and heavy metals, forensic science has shown a growing interest in the detection of organic gunshot residues (OGSR). Despite GC-MS is still considered the golden standard (1), many LC-MS methods for the detection of OGSR can be found in the scientific literature. There are various references about APCI source operating in negative mode (2) which allow a soft ionization of the analytes and different methods for sample pre-treatment, but, to date, there are few references to the use of the Electrospray source (ESI) (3). Recently, it has been observed an increasing use of mass spectrometry as detection technique. Very common in the literature is the use of SIM (Single Ion Monitoring) as a method of acquisition (1). To our knowledge, there are rare papers reporting the determination of both OGSR and stabilizers in a single chromatographic run.

Now, thanks to the coupling of high-performance liquid chromatography with high resolution mass spectrometry (UHPLC-HRMS) it is possible to achieve an innovative instrumental method that allows the simultaneous analysis of the most common OGSR and the four most used stabilizers (DPA, AK-II, EC and MC). The 13 compounds were chromatographically separated by means of a Polar-C18 column. A chlorinated compound was added to the mobile phases, allowing to reveal the adducts with the chlorine. The ion source used in this work is an H-ESI operating in positive and negative combined mode to allow the best conditions for each of the analytes. The revelation was conducted with a high-resolution mass spectrometer with Orbitrap technology that allowed us to work in Full-dds acquisition mode, so as to be able to detect both the parent molecules with and without the adduct with chlorine, and also the most intense fragments of the more stable compounds.

We are applying this method to the determination of GSR and stabilizers on forensic samples collected in crime scenes.

Insert references in brackets as follows: (1) (1, 2, 3) and add reference list at the bottom of the abstract using justified Times New Roman 10, with line-spacing 1. As indicated below at the bottom of the template.

References: 1. T K. Badjagbo, S. Sauve; Critical Reviews in Analytical Chemistry, 42 (2012), pp 257-271. 2. E. Holmgren, H. Calsson, P. Goede, C. Crescezi; Journal of Chromatography A, 1099 (2005), pp 127-135. 3. D. Perret, S. Marchese, A. Gentili, R. Curini, A. Terracciano, E. Bafile, F.S. Romolo; Chromatographia 68 (2008), pp 517–24.

WS1 KN03

Nanobiosensors for diagnostics: from health, environment to safety and security applications

Arben Merkoçi

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There is a high demand to develop innovative and cost effective devices with interest for health care beside environment diagnostics, safety and security applications. The development of such devices is strongly related to new materials and technologies being nanomaterials and nanotechnology of special role. We study how new nanomaterials such as nanoparticles, graphene, nano/micromotors can be integrated in simple sensors thanks to their advantageous properties. Beside plastic platforms physical, chemical and mechanical properties of cellulose in both micro and nanofiber-based networks combined with their abundance in nature or easy to prepare and control procedures are making these materials of great interest while looking for cost-efficient and green alternatives for device production technologies. Both paper and nanopaper-based biosensors are emerging as a new class of devices with the objective to fulfil the “World Health Organization” requisites to be ASSURED: affordable, sensitive, specific, user-friendly, rapid and robust, equipment free and deliverable to end-users. How to design simple paper-based biosensor architectures? How to tune their analytical performance upon demand? How one can couple nanomaterials such as metallic nanoparticles, quantum dots and even graphene with paper and what is the benefit? How we can make these devices more robust, sensitive and with multiplexing capabilities? Can we bring these low cost and efficient devices to places with low resources, extreme conditions or even at our homes? Which are the perspectives to link these simple platforms and detection technologies with mobile communication? I will try to give responses to these questions through various interesting applications related to protein, DNA and even contaminants detection all of extreme importance for diagnostics, environment control, safety and security.

WS1 KN04

Innovative layered materials as active allies for the decontamination of toxic chemical agents

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The oxidative abatement of pollutants and toxic chemical warfare agents (CWA) is conventionally achieved via stoichiometric reactions based on the use of strong oxidants with high environmental impact or via thermal degradation. In this contribution, synthetic and natural clays able to promote selective oxidation reactions to transform toxic CWA in non-noxious products with reduced environmental impact are proposed. Clays, from both natural and synthetic origins, have indeed proved to be suitable materials for the effective decontamination of highly hazardous compounds also thanks to the possibility to properly adapt their chemical properties, either by modifying the the species present in the interlayer space or the framework composition.

In this respect, we have shown that the introduction of aNb(V) species in the framework of saponite clay results in a potential catalyst for the CWA oxidative abatement (Fig. 1). The synthesis method was modified to allow the insertion of Nb(V) ions within the inorganic framework of the clay, thus obtaining a bi-functional catalyst with strong oxidizing properties (due to the presence of Nb(V) centres) and acid character (due to Brønsted acid sites of the saponiteclay)[1]. The catalytic properties of these solids were evaluated at room temperature in the oxidative degradation, with H_2O_2, of (2-chloroethyl)ethyl sulfide (CEES), an organic compound whose chemical structure and reactivity is similar to that of sulfur mustard but with reduced toxicity. Nb-SAP sample is able to transform selectively 80% of CEES in less than 8 h. Moreover, tests performed on the real blistering agent (2,2'-(dichlorodiethyl)sulfide, sulfur mustard, HD agent) showed that the catalysts has a good activity also on the live CWA, under stringent conditions, being able to decompose more than 90% of the sulfide in *ca*. 50 hours. The possibility to add specific functionalities (*i.e.* lanthanide ions) to obtain multifunctional solid with both optical detection and decontamination capabilities will be also shown.

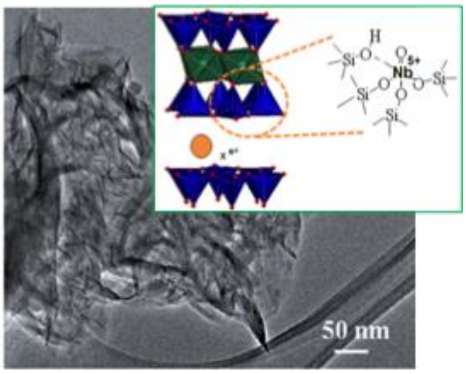

Fig. 1 HR-TEM image of synthetic Nb-saponite

Largely available bentonite from natural origin (containing at least 80 wt% of montmorillonite clay) have been also used to obtain catalyst active for the oxidation of CWA[2]. The bentonite was firstly modified by introducing iron species and acid sites in the interlayer space, aiming to obtain a sorbent with strong catalytic oxidizing and hydrolytic properties. Moreover, a new decontamination formulation was obtained by mixing sodium perborate, as a solid oxidant, to iron-bentonite catalysts. Solid-phase decontamination tests, performed onto a cotton textile support contaminated with organosulfide and organophosphonate simulant agents revealed the good activity of the solid formulation, especially in the in situ detoxification of blistering agents. Tests carried out on HD agent, under ambient conditions, with a 14:1 solid to CWA weight ratio, showed that, thanks to the co-presence of the iron-based clay together with the solid oxidant component, a good decontamination of the test surface from the real warfare agent could be achieved (80% CWA degradation in 24 h).

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WS1 KN05

Photocatalysis versus Plasma-coupled catalysis for the mineralization of warfare and harmful compounds

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Most of the warfare and harmful compounds are resistant to natural degradation and threaten the environment. Therefore, their mineralization emerged as a logical environmental solution. In addition, since their composition includes elements of importance as carbon, phosphorus, sulfur, etc. the product of mineralization may represent a source for these elements. Chemical mineralization requires additional compounds, and therefore, beside the costs of their production it raises a supplementary concern related to potential pollutant effects during either the treatment or recovery of the final products. In this respect, photocatalysis and plasma emerged as potential green solutions. The first one requires a material able to absorb the light energy allowing the separation of charges and on this basis the activation of a molecule able to undergo secondary reactions and to produce mineralization, while the second generates a mixture of electrons and radicals capable to induce the same effects. Photocatalysis is more efficient under atmospheric conditions while plasma offers advantages for the mineralization of these compounds directly in water.

The lecture will provide evidences of the efficiency of the two procedures. Firstly, photocatalysis will consider two different approaches: i) organic sensitizers entrapped in pore-controlled inorganic carriers as zeolites [1] and ii) nitrogen [2] or 3d transition metals doped titania-silica photocatalysts [3, 4]. The effect of further addition of gold nano-particles to these catalysts upon the photocatalytic activity has also been evidenced [5, 6]. The behavior of these catalysts was well correlated to their capability to produce surface singlet oxygen [7]. All these properties were proved in the mineralization of a series of chemical warfare like soman, VX and yperite.

The second procedure will consider the application of non-thermal plasma generated in electrical discharges in liquid or at the gas-liquid interface for the mineralization of dangerous chemicals existing in water. Examples of herbicides, dangerous chemicals and pharmaceuticals will be analyzed [8-12].

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WS1 KN06

Hypothesis of remote identification of warfare chemical agents and explosives after blast of chemical bombs

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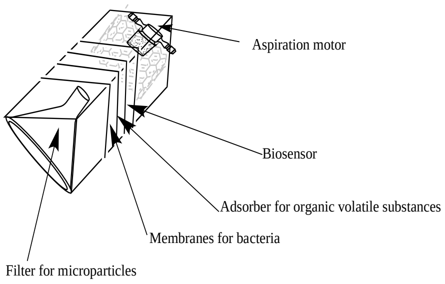
Chemical warfare (CW) involves using the toxic properties of chemical substances as weapons, but, in order to diffuse toxic substances, conventional explosives can be used as well. An improvised chemical dispersal device (ICDD) or "chemical dirty bomb", is composed by different components, mainly the tank containing toxics substances and the explosive charge. Upon impact, the trigger sets off the bomb and disperse the chemical hazardous agent (1). Terrorist attacks can be carried out using chemical warfare agents, according to a statement by CIA director, George Tenet in 2000, according to which Hamas has pursued the capability to conduct chemical terrorism (2). In this perspective, it is important to establish, in addition to the type of chemical agent present in the bomb, what type of explosive has been used, aiming at understanding the origin of explosive matter and helping the investigators to localize the criminal source in case of terrorism attack, or to identify the industrial manufacture which the explosive comes from, in case of war.

After an attack by ICDD, at the place of the event, threatening amounts of extremely toxic chemicals can be present, especially when persistent agents were employed (3). A convenient option is to pick up samples in-situ by using remote flying devices, such as "sampling tool" mounted on board of a drone. The collected sample can be then analyzed by means of a large variety of conventional physico-chemical laboratory techniques, which may provide several details: intact explosive material can be usually identified, with an indication on the manufacturer and/or trade name. Identification of post-explosion residues provides also information about the energetic material used in the explosive device.



The hypothesis aims at building a miniaturized multi-absorber device to aspirate microparticles and volatile substances present at the explosion site, in the view to perform an ex-situ laboratory analysis on the samples to establish the type and the origin of the explosive substance and the nature of chemical agent used in the attack.

The device is sketched in the figure. The solid microparticles are collected and can subsequently undergo SEM analysis and bench-top instrumental characterisation (4); bacteria are collected by a 0.22 μm membrane; organic volatile compounds are collected by active sampling, pumping air through a sorbent layer (at a rate of ca. 10–100 mL min^{-1}) for some minutes (5); the last section is equipped by a biosensor specific for highly toxic nerve CW agents (6).

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WS1 KN07

Early and on site detection of chemical and biological warfare agents using miniaturised electrochemical biosensors

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The availability of analytical tools for fast and in situ detection of warfare agents is a huge issue for the management of suspected area and in case of terroristic attacks. Sensor technology allows to design sensors easily to be integrate in miniaturised devices for in field and fast analysis by unskilled personnel. Herein, the research activity deals with the development of printed electrochemical biosensors for biological and chemical warfare agents will be presented.

In the case of biological warfare agents, we report an impedimetric DNA-based aptamer sensor for a single-step detection of B. anthracis spore simulant (B. cereus spore). Specifically, we designed a miniaturized label-free aptasensor for B. cereus spores based on a gold screen-printed electrode functionalized with B. cereus spores-binding aptamer (BAS-6R). Under the optimized conditions, the developed aptansensor demonstrated its capability to detected B. cereus spores 14579 with a linear range between 10^4 CFU/ml and 5×10^6 CFU/ml and a detection limit of 3×10^3 CFU/ml. Furthermore, the study of selectivity toward B. cereus 11778, B. subtilis, Legionella pneumophila, and Salmonella Typhimurium demonstrated the capability of this sensor to detect B. cereus spores, proving the suitability of the DNA-based sensing element combined with a portable instrument for a label-free measurement on site of B. anthracis spore simulant (1).

In case of chemical warfare agents, we developed a miniaturised biosensor for Sarin gas detection (2), which was also embedded in a lab-on a chip for easily monitoring of contaminated area (3).

Herein, we reported the first example of a fully-integrated paper-based electrochemical biosensor able to detect nerve agents exploiting screen-printing technology to print the electrochemical cell on paper as well as wax printing for paper based microfluidics. The use of paper reduces the costs of fabrication as well as the impact of the environment. In addition, the paper-based sensor after the measure can be easily incinerated, improving the sustainability in the waste management. This biosensor is based on the use of butyrylthiocholine as a substrate being able to provide an electroactive by-product, thiocholine. We exploited nanocomposite constituted of carbon black (CB)/PB nanoparticles for thiocholine detection since it is able to electrocatalyse the oxidization of thiol-containing compounds at low applied potential with high sensitivity. Furthermore, the porosity of the paper wax exploited to load the reagents required for the measurement, allowing for a reagent free device. This biosensor was challenged towards paraoxon (nerve agent simulant), achieving a detection limit of 3 μg/L (4). For the mustard agent detection, recently we have developed a paper-based bioassay based on the choline oxidase inhibition, using 2-chloroethyl ethyl sulfide as simulant (5). Herein, we present the results obtained in the development of an origami paper-based device for mustard agents ready to use and its applicability was demonstrated for the rapid and real-time detection of real sulfur mustard, obtaining limits of detection equal to 1 mM and 0.019 g·min/m^3 (6).

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WS1 KN08

Working for the Chemical Weapons Convention: interdisciplinary expertise and funding opportunities

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The Chemical Weapons Convention (CWC) is an international treaty ratified by 193 states which not only provides for a comprehensive ban of chemical weapons, including their development, production and use, but also offers numerous opportunities to States Parties to cooperate in protection and security areas, legal, scientific, technological, and other spheres.

The Organisation for the Prohibition of Chemical Weapons (OPCW), the winner of the Nobel Peace Prize in 2013, which was established as an implementation agency for the CWC at its entry into force in 1997, implements a unique industry verification regime to ensure the non-proliferation of chemical weapons, investigates on the cases of non-compliance, and monitors the developments in science and technology. It has been instrumental in promoting chemistry for peace, education and outreach to stakeholders and general public, while facilitating political debates and stimulating dialogue and cooperation amongst stakeholders to ensure the full eradication and non-re-emergence of this deadly category of weapons of mass destruction.

In the framework of the implementation of Article XI of the CWC (the peaceful uses of chemistry), the International Cooperation Branch of the OPCW is running a series of programmes tailored for various stakeholders, mainly industry, research and academia: to enhance their capacity in the field of analysis of chemicals subject to the CWC; to support scientific research in the areas of relevance to the CWC; to promote the culture of chemical safety and security; and to streamline ethics, education and gender issues. Such programmes are mainly intended to benefit Member States which either developing countries or those with economies in transition. This component of the OPCW work closely addresses the development goals of MSs and is synergetic to UN SDGs; yet it is now seen among the future priorities in the OPCW as the chemical disarmament is closing to an end.

WS1 - Oral Communications

- **WS1 OR01 -** Lidietta Giorno - CNR-ITM, Rende, Italy *“Biocatalytic membrane reactors for organophosphates degradation”*
- **WS1 OR02 -** M. Maddalena Calabretta - Department of Chemistry “G. Ciamician”, University of Bologna, Italy *“Origami paper-based chemiluminescent biosensor for neurotoxic compounds detection using an integrated smartphone device”*
- **WS1 OR03 -** Gaetano Carminati - Senior Technical Expert from the National Authority for the Prohibition of Chemical Weapons, Rome *"The role of the Italian National Authority"*
- **WS1 OR04 -** Lai Van Cuong - Centre of Environmental Treatment Technology, Chemical Core, Ministry of National Defence, Hanoi *“Lessons learnt and identified issues related to CBRN Joint Field Training Exercise in ASEAN Nations”*
- **WS1 OR05 -** Simona Ortelli - CNR-ISTEC, Faenza, Italy *“Coatings based on* TiO_2 *nanoparticles and biomacromolecules as a new flame retardant approach for cotton fabrics”*
- **WS1 OR06 -** Salvatore Corrao - Italian Fire Brigade Corps, Italy *“Study of an organizational model for the operational response of an Italian CBRN Module within the European Civil Protection Mechanism”*
- **WS1 OR07 -** Daniele Del Gaudio - Italian Army, Italy *“7th CBRN defense regiment “Cremona” a special unit against CBRN events”*
- **WS1 OR08 -** Ferruccio Trifirò – Università degli Studi di Bologna, Accademia delle Scienze dell’Istituto di Bologna, Italy *“How to avoid dual-use toxic substances in chemical industry”*
- **WS1 OR09 -** withdrawn
- **WS1 OR10 -** Federico Begni - University of Eastern Piedmont, Alessandria, Italy *“Hyper cross-linked polymers for the removal of harmful pollutants from the environment”*
- **WS1 OR11 -** Isacco Gualandi - University of Bologna, Italy *“Detection of hazardous chemicals (pesticides) by electrochemical sensors”*
- **WS1 OR12 -** Andrei Katsev - Medical Academy Georgievsky, Simferopol, Crimea *“Detection of the toxicity of environmental and pharmaceutical substances by luminescence biotests”*
- **WS1 OR13 -** Stefano Scaini - Senior Safety & Security Advisory, Italy *“Unconventional use of High Explosives & Energetic Materials: facing the I.E.D.s Threat”*
- **WS1 OR14 -** Davide Janner - Politecnico di Torino - Department of Applied Science and Technology *“Nanostructured gold surface for reliable and low-cost SERS detection of contaminants in water”*
- **WS1 OR15 -** Rosalind Sankey and Carlos Rodriguez Del Rio – Elsevier *“Using information solutions to understand the potential risks and control strategies of substances”*
- **WS1 OR16 -** Davide Vignola - Pollution Analytical Equipment, Italy *“Detection of highly toxic chemicals, explosives and explosive taggants in the air”*
- **WS1 OR17 -** Stefano Marchesi - University of Eastern Piedmont, Alessandria, Italy *“Bi-functional Eu(III) and Nb(V)-containing Saponite Clays for the Optical Detection and Catalytic Abatement of Chemical Warfare Agents”*
- **WS1 OR18 -** Murugiah Muthusamy - Fire & Rescue Training Academy, Malaysia *“Strategies for analysis of chemical weapons for forensic and legal prosecution”*
- **WS1 OR19 -** Antonio Sergio - New DuPont, Italy *“For greater good”*

- **WS1 OR20 -** Gianmaria Pio - Department of Civil, Chemical, Environmental and Materials Engineering DICAM, University of Bologna, Italy *"Fire security and safety of chemical warehouses"*

WS1 OR01

Biocatalytic membrane reactors for organophosphates degradation

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The health risks represented by organophosphates compounds (pesticides and nerve agents) and the need for their detection and disposal pushes research towards new processing strategies having high efficiency and environmental sustainability. Enzymatic reactions owing to their specificity, efficiency and low energy consumption are excellent candidates to reach this goal. Membranes are optimal supports for enzyme immobilization because a separation process can be coupled with the enzyme-mediated conversion and the immobilization process can improve enzyme stability.

This work discusses a biocatalytic membrane reactor (BMR) containing an immobilized phosphotriesterase (PTE) for the degradation of organophosphates. Paraoxon has been used as a model contaminant to evaluate the performances of the system. In order to develop BMR able to decontaminate organophosphate contained in liquid or gas phase different membrane materials where functionalized and evaluated for phosphotriesterase covalent immobilization. In particular, a hydrophobic membrane made of polyvinylidene fluoride (PVDF) and two hydrophilic membrane made of polyethersulfone coated with polyethyleneimine (PES-PEI) and regenerated cellulose (RC) were used. Surface modification of PVDF flat-sheet membranes was performed using 1,5-diamino-2-methylpentane (DAMP), as carrier of amino groups (1). The RC membrane was modified by oxidizing the hydroxyl groups of the glucose units into aldehydes which were subsequently derivatized with ethylenediamine (EDA). Afterwards, the amino groups of modified PVDF, PES-PEI and RC membranes were reacted with an aqueous glutaraldehyde (GA) solution in order to bind PTE in mild conditions. The PTE-loaded membranes were characterized in terms of enzyme-loading, catalytic activity, enzyme spatial distribution within the membrane, vapour and water permeability. The catalytic activity and stability of the three different biocatalytic membranes were investigated using each enzyme-loaded membrane cut in small pieces in a stirred tank reactor. In this system the transport of the reagent/product occurred by diffusion. The RC biocatalytic membrane, which showed the best performances in liquid phase, was then used to build the biocatalytic membrane reactor, where reagents transport and product removal occurred mainly by convection (2). The BMR worked as a continuous stirred tank reactor and was able to achieve about 90% of paraoxon degradation at each passage of the contaminated stream through the biocatalytic membrane. The immobilized PTE maintained good catalytic efficiency for repeated uses over a period of about 6 months of observation, under operating and storage conditions, retaining more than 70% of specific activity. On the other hand, the free PTE showed a half-life time of about 1 month.

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WS1 OR02

Origami paper-based chemiluminescent biosensor for neurotoxic compounds detection using an integrated smartphone device

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Global security threats have become a major worldwide concern and their early and sensitive detection represents a major challenge to current monitoring technologies. The routine monitoring of water, food and the environment for chemical and biological threat agents is often hampered by the fact that available techniques usually require clean samples and sophisticated equipment based on high performance liquid chromatography-tandem mass spectrometry and are thus unsuitable for real-time, cost-effective and on-field routine monitoring. Here, we report the development and optimization of a novel origami paper-based chemiluminescent (CL) biosensor for acetylcholinesterase activity detection and its implementation into portable analytical devices as proof-of-principle of low-cost point-of-care applications. This biosensor is based on the inhibition process of acetylcholinesterase (AChE) by molecules such as pesticides, nerve gases and some drugs in which activity of AChE is measured through a series of coupled enzymatic reactions leading to light emission. When acetylcholinesterase is inhibited, there is a decreased production of hydrogen peroxide, and consequently a reduction in light emission. In particular, three different enzymes, AChE, choline oxidase (ChOx) and Horse Radish Peroxidase (HRP), involved in the chemical reaction are adsorbed on the paper PAD obtained by wax printing. Due to the its high affinity, tacrine, a competitive reversible inhibitor of AChE, was used as model analyte (concentration range 1 – 1000 μM). Hydrogen peroxide is produced based on the presence or absence of harmful substances acting on AChE. Signal acquisition was carried out by OnePlus 5 photocamera placing the 3D paper PAD cartridge inside a dark box and integrating CL signals for 30 sec with ISO3200 (Fig. 1).

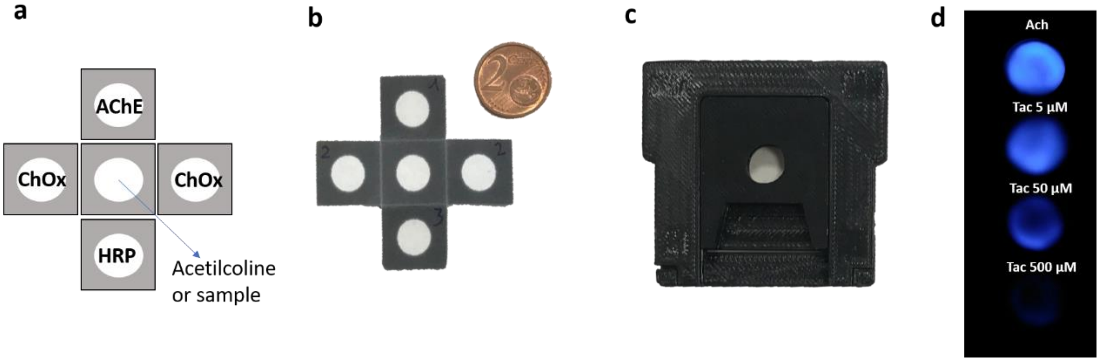

Fig. 1: a) schematic representation of origami paper-based chemiluminescent biosensor and b) paper PAD obtained by the wax printing technique; c) 3D paper PAD cartridge d) CL signals acquired with OnePlus 5 smartphone.

Conscious that huge efforts will be required to extend the stability of the origami paper based biosensors without affecting the analytical performance of the system, we believe that, once optimized, it could find significant application as rapid alerting tool, suitable for detecting the presence of harmful pollutants in civil and military water supplies, for terrorism surveillance, and for detection of health threats in drinking water in developing countries.

WS1 OR03

The role of the Italian National Authority

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Since the enter into force of the Chemical Weapons Convention, CWC, Italy, as a State Party, through the Law no. 496, implemented the National Authority and the build-up of national organisation. Along 22 years of work, the Italian National Authority has provided a constant support to the Technical Secretariat of the Organisation for the Prohibition of Chemical Weapons, OPCW, in the of training of inspectors, during the Sirian and Lybian chemical disarmament process, but also in the promotion of peaceful uses of chemistry with seminar activities, summer schools and exchange programmes devoted to young chemists in chemical industrial site at worldwide level.

Since 2016, the CWC has been promoted in national universities and academic environments in order to encourage a wider working opportunity offer by the OPCW as well as the possibility to strengthen a better scientific knowledge and expertise on these topics.

WS1 OR04

Lessons learnt and identified issues related to CBRN Joint Field Training Exercise in ASEAN Nations

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WS1 OR05

Coatings based on TiO_2 nanoparticles and biomacromolecules as a new flame retardant approach for cotton fabrics

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The burning of textiles has always been considered a major hazard: indeed, most fibers and fabrics, which play an important role in everyday life (e.g. for transportation, automotive industry, protective garments, the military, furniture upholstery, bed linen and nightwear), are flammable and potentially dangerous materials (1). As a consequence, chemical species (so-called flame retardants - FRs) have been developed in order to limit the risk of fire, by inhibiting the fabric ignition or reducing the rate of flame spread. Thus, the flame retardant finishing, that can be counted among the most important textile finishes, and is undoubtedly the noblest technical treatment.

A novel durable intumescent flame retardant coating, based on metal oxide nanoparticles (NPs) and biomacromolecules, was designed and applied on cotton fabrics. This way, it was possible to combine the thermal insulating effect of the inorganic coating with the intumescent properties of the selected biomacromolecules (whey proteins, caseins and DNA), able to absorb the heat and oxygen from the atmosphere and blocking their transfer to the surrounding textile (2). Two peculiarities were exploited, namely: i) the ability of proteins and aminoacids to irreversibly cover NPs, according to protein corona theory and ii) the affinity of metal oxide NPs towards the natural hydrophilic fibers, for improving the washing fastness of the fire-resistant finishing. To this aim, different hybrid TiO_2 NPs/biomacromolecules systems were deposited by dip-pad-dry-cure process and the morphology of the resulting coating assessed by SEM analysis. The enhancement of the durability (i.e. the resistance to washing treatments) was verified by release tests carried out in static and dynamic conditions (3, 4). Flammability and cone calorimetry tests were performed for evaluating the fire behavior of the treated fabrics. The resulting flame retardant features confirmed that the hybrid titania/biomacromolecules coatings are able to decrease the burning rate (even achieving self-extinction in the case of DNA and caseins, Figure 1), as well as to decrease HRR, PHRR and THR and to increase the final residue, thus indicating the protection effect exerted by the deposited char forming coatings. Therefore, thanks to their high char-forming character, the combination of TiO_2 nanoparticles and biomacromolecules within coating may represent a valid durable fire-resistant finishing alternative to standard flame retardant treatments for cotton.

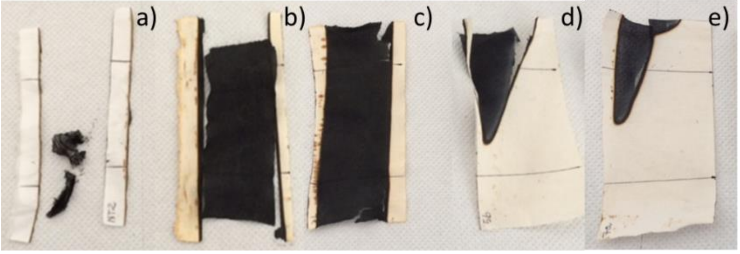

Figure 1. Residues after horizontal flame spread tests: a) untreated cotton, b) TACR/DNA (8 layers), c) TACR/DNA (4 layers), d) TiO_2CIT/DNA (8 layers) and e) TiO_2CIT/DNA (4 layers).

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WS1 OR06

Study of an organizational model for the operational response of an Italian CBRN Module within the European Civil Protection Mechanism

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The purpose of this paper is to show the state of the art of the European Civil Protection Mechanism and how the National Fire Service (CNVVF) in Italy - as a fundamental component of civil protection (1) - is included in the management of interventions and out-of-area operations in the CBRN/HAZMAT area. The work intends to define an intervention proposal following acceptance of the European CBRN Module of the CNVVF within the CECIS (Common Emergency and Information System) database at the ERCC - Emergency Response Coordination Center in Brussels (2). In fact, the intent of this work is to define an organizational model - ready on demand - with resources in terms of men, means, materials pieces of equipment for interventions or management of HVE (High Visibility Events) in and off from Italy (3). In the past, the activation of pseudo-modules or pseudo operational packages saw the participation of the National Fire Service in events such as Haiti earthquake and in international exercises, which will be mentioned in this work.

Going through the paper, the intent is also to provide an overview of the skills and expertise present in the CNVVF in the specific CBRN sector (4) and show the adherence of these to the prescriptions of the Council Decision on the European Civil Protection for a CBRN Module. Some follow-up are the results achieved, the feedbacks, the lessons learned from international exercises where the Italian Fire Brigade took part and, finally, an Operational Response Proposal of the Module followed by the ERCC of Brussels through the Fire Service National Operative Center, seeing also the deployment of aircraft, like “Piaggio P.180 Avanti”, an Italian executive transport aircraft.

To conclude, the present work tends to update the documentation on the subject, constituting a possible didactic resource for the training of the operational personnel from CBRN Regional Units that will participate in international interventions in the future. This personnel must be able to know the intervention standards described in handbooks (INSARAG, UNDAC, ...) (5) and provide information to t contact officers (Liaison Officers) who follows the activities of international coordination at LEMA (Local Emergency Management Authority) and OSOCC (On-Site Operations Coordination Center (6).

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WS1 OR07

7th CBRN defense regiment "CREMONA" a special unit against CBRN events

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The nightmare scenario is that these terrorists get their hands on CBRN materials or WMD. The physical, economic and psychological effects of such an attack – even one on a relatively small scale – would be devastating. Increased CBRN know-how, the spread of the appropriate tech and expertise, and the growing capabilities of terrorist groups present a serious threat (1). The 7th CBRN defense regiment is the only regiment capable of dealing with a CBRN threats. On the national territory the regiment competes with the civil authorities in the decontamination e monitoring of sites involved in CBRN events, in operational theatre implements the assistance measures for the population and the army in order to guarantee their survival from the threats.

For these tasks the regiment makes use of specialized units for the detection, identification and confirmation of the CBRN materials.

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WS1 OR08

How to avoid dual-use toxic substances in chemical industry

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In this note I shall report some examples on the elimination from chemical industry of substances that can be toxic for workers and population, close to the plant where they are produced and used. These substances can be also used as chemical weapons. The substances examined are: HCN, $COCl_2$ and Cl_2. HCN can be used for the production of acrylonitrile by reaction from acetylene, but nowadays it is produced by reaction of ammoxidation of propylene and, in the future, through the ammoxidation of propane, so to avoid the coming back to the use of HCN, due the gradually increasing prize of propylene. Adiponitrile is produced mainly by reaction of butadiene with HCN, but it can substituted by electrochemical dimerization of acrylonitrile synthesized using propane ammoxidation as well. Methacrylic acid is produced by reaction of acetone with HCN, but this reaction can be substituted by direct oxidation of isobutane or isobutene. Aromatic nitriles can be produced by reaction of alkylaromatics with cyanides or HCN, but these reactions can be substituted by ammoxidation with NH_3. Chlorine is used in the epoxidation of propylene via formation of epichloridrine, but this reaction can be substituted by epoxidation with hydroperoxides or H_2O_2. Chlorine can be used as intermediate in the production of fluorides from olefins, but it can eliminated by reaction of direct oxyfluorination of olefins. Phosgene is used in the production of polyurethanes and polycarbonates but these reactions can be substituted by: reductive carbonylation (reaction between nitroaromatics and CO); oxidative carbonylation (reaction between aromatic ammines and CO and O_2); reactions of ammines with with dimethylcarbonate.

WS1 OR10

Hyper cross-linked polymers for the removal of harmful pollutants from the environment

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**Corresponding author*

In the last years, pollutants removal from the environment has proven to be an important and expensive task. Among the different remedies which can be employed to address this problem the use of solid adsorbents is highly recommended due to its low cost and easy operation. In this work, we studied and compared the adsorption capacities of toluene (chosen as representative of aromatic molecules) on different materials including well established adsorbents, such as zeolites and mesoporous silica and novel hyper cross-linked polymers (HCPs). HCPs were prepared by modifying the method reported in the literature and using different ratios between monomer tetraphenylmethane (TPM) and cross – linker, formaldehyde dimethyl acetal (FDA) (1). Synthetic route for HCPs consists of employing a Friedel – Crafts alkylation using $FeCl_3$ as catalyst to promote the formation of a rigid, highly cross-linked framework. By using different TPM/FDA ratios, materials with a different degree of cross-linking are obtained, possessing specific surface area of 1236, 1289 and 1318 m^2/g and pore volume of 0.78, 0.96 and 1.06 cc/g respectively for ratios of 1/9, 1/16 and 1/30. Adsorption data showed much higher toluene uptake for HCPs with respect to zeolites and silicas (in particular, Y and MCM-41 solids) also thanks to the swelling properties of the polymeric framework. The nature of host-guest interactions has been studied by combining FT-IR and SS-NMR spectroscopy and following the adsorption of fully deuterated toluene. By combining volumetric analysis and spectroscopy methods it was derived that the organic nature of the aromatic framework displayed by HCPs, together with their high surface area, are key properties to improve significantly the toluene adsorption capacities.

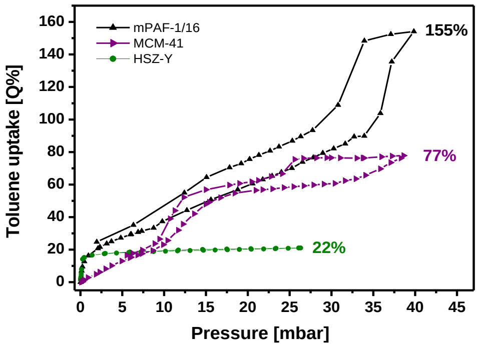

Figure 1. Adsorption isotherms of toluene, at 308 K, adsorbed on HCP UPO-1/16 compared with Zeolite Y and silica MCM-41.

Reference 1. M. Errahali, G. Gatti, L. Tei, G. Paul, G. A. Rolla, L. Canti, A. Fraccarollo, M. Cossi, A. Comotti, P. Sozzani and L Marchese. J. Phys. Chem. 2014, 118, 28699‒28710.

WS1 OR11

Detection of hazardous chemicals (pesticides) by electrochemical sensors

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Among herbicides, glyphosate (Glyp) and glufosinate (Gluf) are both organophosphorus compounds with broad-spectrum systemic actions. The intensive use of these herbicides generates concerns regarding their impact in environment and their possible health hazards. They are usually quantitated by expensive chromatographic equipment interfaced with a mass spectrometer detector. Electrochemical sensors represent a good and innovative alternative in term of on-site detection, sensitivity, rapid response, and miniatured size for the determination of these pesticides.

Modified electrodes based on electrodeposited Ni/Al Layered Double Hydroxides (LDHs) have been used to detect Glyp and Gluf, in one step. In particular, Glyp and Gluf determinations were realized under hydrodynamic conditions at a rotating disk electrode at E_{app} = 0.49 V vs SCE, in 0.1 M NaOH solutions, exploiting the ability of the redox couple Ni(III)/Ni(II) to act as redox mediator for the oxidation of the amino group (1). The sensors presented a very stable and rapid current with an average response time of 20 s. For Glyp determination the response was linear between 0.01 and 0.9 mM with a detection limit (LoD) of 1 μM and sensitivity of 287 mA/M cm^2.

This contribution also describes an electrochemical biosensor based on glassy carbon electrodes (GCE) modified with a composite material composed by graphene oxide (GO) and multi-walled carbon nanotubes (MWCNTs). Alkaline phosphatase (ALP) was used as recognizing agent and was immobilized on the electrode surface with a membrane obtained with bovine serum albumin and glutaraldehyde. Before enzyme deposition, the composite material was reduced by cyclic voltammetry (CV) to partly restore the graphene conductivity features. ALP can dephosphorylate ascorbic acid phosphate (AAP) to form ascorbic acid which is easily detected at the modified GCE by CV or amperometry. Some herbicides and pesticides inhibit ALP activity and thus this process can be exploited for their detection. Figure 1 shows the voltammogram recorded in Tris buffer containing 3 mM AAP and 2,4-dichlorophenoxyacetic acid (2,4-D) as inhibitor, at different concentrations, that leads to a decrease of AAP signal. Since each inhibitor molecule hinders the dephosphorylation of many AAP, its chemical signal is amplified, as demonstrated by the LoD (2 pM) which is much lower than the one usually achievable by CV. Finally, we have demonstrated the general approach by testing different pesticides and we are trying to embed this system in an organic electrochemical transistor to obtain a sensor with boosted performances.

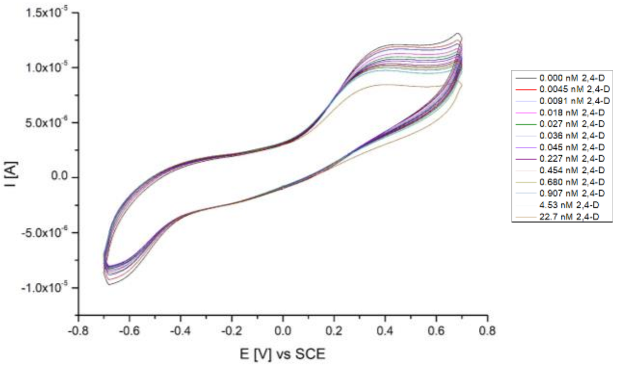

Figure 1. Voltammograms (0.05 V s^{-1}) recorded in Tris buffer containing 3 mM AAP and different amounts of 2,4-D herbicide.

Reference: 1. A. Khenifi, Z. Derriche, C. Forano, V. Prevot, C. Mousty, E. Scavetta, B. Ballarin, L. Guadagnini, D. Tonelli, Analytica Chimica Acta 654 (2009) 97–102.

WS1 OR12

Detection of the toxicity of environmental and pharmaceutical substances by luminescence biotests

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The state of the environment is considered to be one of the most important objects for early investigation and analysis in terms of ensuring and maintaining the quality of Life. A large amount of chemical, biological and other methods is being developed to assess multifaceted ecological risks and threats. Recently, a new universal bioanalytical technology applicable for the detection toxic properties of environmental samples, synthetic and natural substances, materials of different nature, including nanosized and nanostructured ones was described [1]. This technology includes several stages based on a unique common principle: the evaluation of the metabolic activity of bioluminescent test-microorganisms by means of physical signal and intensity of their bioluminescence. Such approach was called as bioluminescent analytical technology (BAT). On its first step, natural bioluminescent bacteria or recombinant ones with constitutive bioluminescence are used in order to reveal the toxic properties of a sample by measuring the level of bioluminescence inhibition. Specific mechanism of the revealed toxicity is studied on the next step of BAT by means of a battery of recombinant luminescent bioreporter strains. The light emission of these test organisms can be influenced by the substances with particular mechanism of biological activity (toxicity), for instance, damaging of nucleic acids, proteins or biological membranes.

This report is focused on the improvement of the first step of the BAT, that leads to a quick assessment of the biotoxic properties of studied samples by monitoring the bioluminescence inhibition. For these purposes, the bioanalytical potential of new luminescent bacteria collected in Black and Azov seas was studied. Twelve strains of marine light-emitting bacteria were isolated from the samples of coastal water and hydrobionts, gathered in different areas of the Black and Azov seas, with differences in salinity and depth. Obtained bacteria were studied and identified at the species level by means of phenotyping methods, as well as specific biophysical and biochemical approaches. Additionally, molecular genetic techniques were utilized for a detailed taxonomic study. The sensitivity of the isolated luminescent bacteria towards the action of various model toxicants was estimated and three luminous strains belonging to the *Photobacterium leiognathi* species were revealed for promising practical applications as whole-cell bacterial biosensors.

These strains were, for instance, applied in practical purposes to analyze the toxic properties of environmental pollutants, such as heavy metals, organic compounds. Particular group of studied materials were nanosized and nanostructured inorganic metal oxides, that recently proved to be suitable catalysts for the oxidative decontamination of chemical warfare agents [2]. Bioluminescent bacteria biotests can be also applied as a screening tool for antibacterial properties of new biological active synthetic or natural substances [3].

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2. C. Bisio, F. Carniato, C. Palumbo, S. L. Safronyuk, M. F. Starodub, A. M. Katsev, L. Marchese, M. Guidotti, "Nanosized inorganic metal oxides as heterogeneous catalysts for the degradation of chemical warfare agents", Catal. Today, 277 (2016) 192–199.
3. L.M. Antypenko, S.I. Kovalenko, O.V. Karpenko, A.M. Katsev, V.P. Novikov, N.S. Fedyunina, "1-R-2-([1,2,4]Triazolo[1,5-c]quinazoline-2-ylthio)etanon(ol)s: Synthesis, Bioluminescence Inhibition, Molecular Docking Studies, Antibacterial and Antifungal Activities", Current Computer-Aided Drug Design, 12, 1 (2016) 29-41.

WS1 OR13

Unconventional use of High Explosives & Energetic Materials: facing the I.E.D.s Threat

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The chemistry of High Explosives & Energetic Materials and the physics of the explosion-related phenomenon are well known and allow to take advantage of the characteristics and features of such powerful substances and compounds of.

The most common conventional uses of them concern several applications in the fields of civil, industrial, space, mining and environmental engineering as, for example, controlled blasting demolition of buildings, explosive welding of metals and alloys, explosive metal shaping, tunneling, open pit and underground mining, avalanche control and, thinking to Low Explosives, pyrotechnics (fireworks) and SFX (special effects).

Unfortunately their features are very well known by Non-state Actors and terrorist organizations too, and often used in a dual-use way to boost I.E.D.s (improvised explosive devices) and W.M.D.s (weapons of mass destruction) towards their enemies and targets.

To analyze unconventional weapons and the ways they are able to hit and strike different kinds of target, exploiting the direct and indirect effects of the explosion phenomenon, is basic to mitigate their effects, reducing effectively the threshold of residual risk related to nowadays I.E.D.s Threats.

WS1 OR14

Nanostructured gold surface for reliable and low-cost SERS detection of contaminants in water

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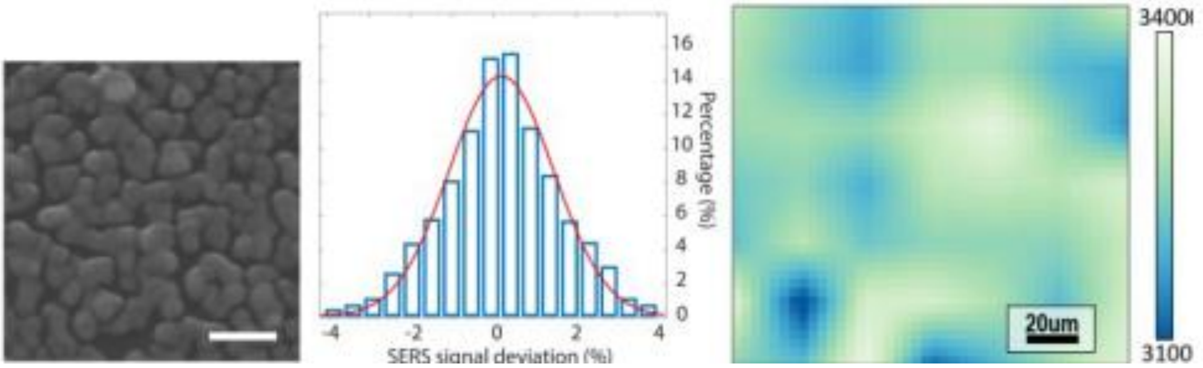
The presence in water of biological contaminants like pesticides, fungicide and polycyclic aromatic hydrocarbons present a serious threat to health and safety of human beings and their surrounding environment influencing the agricultural and food processing industry. In particular, there is a lack of quick analytical tools with enough sensitivity to issue an early warning of contamination in the environment or screening in the agri-food processing and on water treatment facilities. Surface enhanced Raman scattering (SERS) is a technique that can be made sensitive and quick to comply with these requirements (1). While many demonstrations of ultra-high sensitivity detection in SERS have been reported (1,2), mostly these performance leverages on a complicate fabrication via e-beam lithography or on the use of special particles in colloidal form.

In this work, we will present our recent advances in the development of low-cost nanostructured gold surfaces for the detection of contaminants (3) suitable to be used in portable analytical tools. We will show that their sensitivity and accuracy are well beyond the needed detection limits and through a careful engineering of the surface properties we achieve a great uniformity of the distribution of the hotspots reaching a variability of the SERS signal over 100μm x 100μm surface of less than +/-2%.



The fabrication process of the gold nanostructured surfaces is completely obtained by a wet chemistry and consists of three steps: surface functionalization, seed deposition and nanostructure growth. In the surface functionalization we optimized the process to obtain a controlled deposition of gold seed nanoparticles. As shown in the figure, the nanostructure presents a texture that has a high density of crevices that are "hot-spots" where light is confined and the SERS effect takes place.

Moreover, the growth process can occur in an isotropic or anisotropic way allowing to obtain gold nanosurfaces with different nanometric textures that strongly enhance the Raman signal allowing high sensitivity and reliability. SERS performance of the substrate will be presented showing high senisivity for Thiram and Carbaryl (fungicide) and also to detect a dangerous colorant like Sudan III that is banned worldwide for its extree toxicity but still used illegally.

References: 1. Lane, L. A.; Qian, X.; Nie, S. Chemical Reviews, 2015, 115, 10489. 2. J. F. Betz, W. W. Yu, Y. Cheng, I. M. White, G. W. Rubloff, Physical Chemistry Chemical Physics, 2014, 16, 2224 3. EUROPA - Animal Health & Welfare - Animal Welfare - Welfare on the Farm - Ongoing Initiatives.

WS1 OR15

Using information solutions to understand the potential risks and control strategies of substances

[a]Rosalind Sankey and [a]Carlos Rodriguez Del Rio

[a] Elsevier

This presentation will cover the ways in which information solutions, such as Reaxys, can be used to better understand the potential risk that substances pose to human health and the environment. By having a greater understanding of these potential risks, an effective strategy for their control can be devised.

WS1 OR16

Detection of highly toxic chemicals, explosives and explosive taggants in the air

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The technological-industrial risk is associated with the occurrence of events that may be of intentional origin, following terrorist or sabotage action, and of accidental origin, as a result of human error, fire or deterioration of materials. The use of a sophisticated technique such as gas chromatography in mass spectrometry allows identifying in a few minutes a mixture of qualitatively and quantitatively unknown compounds.

The response to threatened or real incidents requires actions in critical and restricted times, therefore it is necessary to carry out a correct assessment of the situation to minimize exposure to harmful agents. A correct evaluation of the consequences of a release of toxic substances cannot be separated from the analysis of the immediate effects on people and infrastructures; these effects are related to measurable chemical-physical quantities, whose knowledge is the basis of the quantitative assessment of the consequences.

HAPSITE ER Chemical Identification System delivers qualitative and quantitative lab-quality results in the field, in less than 10 minutes thanks to the miniaturized GC / MS.

HAPSITE ER is designed as a portable analyzer to be used in case of chemical attack, it is suitable for use in the field even in emergency situations as it is simple to use for even basic skill levels with minimal training. HAPSITE ER is fast thanks to the pre-programmed methods to obtain quality data in minutes with a few simple keystrokes and it can be used in any environmental condition, even in the presence of smoke and dust. Also HAPSITE ER can be easily washed and decontaminated with the most common techniques.

HAPSITE ER SPME Sampling System, attached to the HAPSITE via its universal interface, provides allows to introduce SVOCs into HAPSITE ER. SPME is an effective extraction technique that has been successfully employed in the field for the pre-concentration of a variety of compounds.

Many organic high explosives and explosive taggants do not have a high enough vapor pressure for effective vapor sampling. However, these explosives and their commercial explosive mixtures have characteristic components detectable by GC/MS.

SPME sampling will readily extract these compounds from the air. A study was carried out to evaluate SPME extraction, followed by an introduction to the SPME Sampling System thermal desorption chamber and HAPSITE ER compound detection and identification, of the following explosives taggants: 2-nitrotoluene (2-NT), 3-nitrotoluene (3-NT), 4-nitrotoluene (4-NT), 2,3-dimethyl-2,3-dinitrobutane (DMNB) and common explosives: 2,4-dinitrotoluene (2,4-DNT),
2,6-dinitrotoluene (2,6-DNT), and triacetone triperoxide (TATP). This study demonstrates the increased versatility of HAPSITE ER with the addition of the SPME Sampling System.

WS1 OR17

Bi-functional Eu(III) and Nb(V)-containing Saponite Clays for the Optical Detection and Catalytic Abatement of Chemical Warfare Agents

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It was recently shown that layered smectite clays are good candidates for the abatement and decontamination of chemical warfare agents (CWAs) (1). Clays present several advantages such as high robustness, enhanced adsorption capabilities, good chemical versatility and very low production costs, which make them excellent catalysts for the removal and destruction of CWAs. In particular, saponites bearing in-framework Nb(V) sites (hereafter named Nb-SAP) were successfully employed in the selective oxidative abatement of (2-chloroethyl)ethyl sulfide (CEES), a simulant of sulfur mustard CWA, under mild conditions (1). In this work, we aimed at designing a multifunctional solid with both optical detection and decontamination capabilities. In this respect, Eu(III) centres were introduced in the inorganic framework of NbSAP by properly modifying the synthesis method to allow the incorporation of both Nb(V) and Eu(III) ions in the clay's framework (sample named EuNb-SAP) or in the interlayer space, through ion-exchange process (sample named Eu-NbSAP). Moreover, samples containing only Nb(V) or Eu(III) species were prepared as references (NbSAP and EuSAP samples). All solids were fully characterized from the physico-chemical point of view. Both optical measurements and catalytic tests were carried out organic (*n*-heptane) and in aqueous media. In sensor tests, the Eu(III)-containing saponite clays were able to detect the presence of CEES in the media after few seconds of contact time, as confirmed by a decrease of the intensity of the emission band of Eu(III) at 614 nm ($^5D_0$-$^7F_2$), which is sensitive to the coordination of CEES. The CWA abatement performance was tested in liquid-phase degradation of CEES under batch conditions and followed by UV-Vis, GC-FID/MS and ^{1}H-NMR analyses. It was shown that framework Nb(V) centres and the surface acidity of clays are the key factors at the basis of the oxidative performance of Nb-SAP: the sample is indeed able to decompose more than 80% of CEES in 6 h (Fig.1). The presence of Eu(III) in exchange position did not significantly inhibit the catalytic performance, whereas sample with framework Eu(III) species decomposes *ca*. 70% of CEES in 24h, probably because of the low content of Nb(V) species. In aqueous phase, in particular, both metal sites additionally led to the hydrolysis of the chlorine-containing moiety and to the formation of hydroxy-organosulfur by-products. Further tests with Eu(III)-containing samples with higher amount of Nb(V) were also performed aiming to increase the catalytic performances of clay based samples.

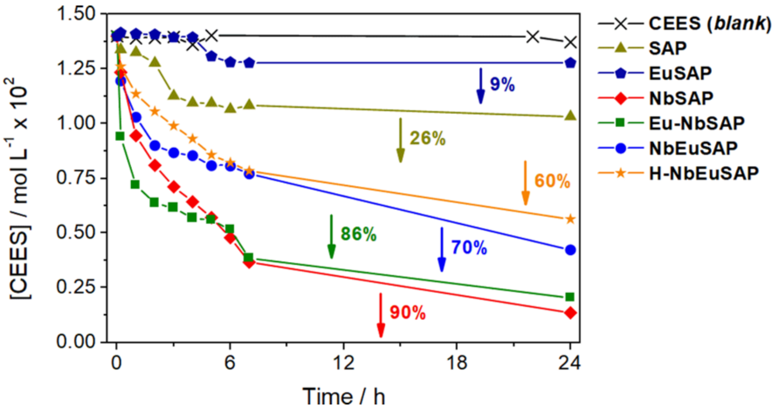

Figure 1. Oxidative abatement of CEES with hydrogen peroxide over different saponite samples containing Eu(III) and/or Nb(V) sites. *Reaction conditions:* 14 mM CEES, 70 mM 30% aq. H_2O_2, phosphate buffer solution (PBS, 10 mM, pH = 7), 20 mg catalyst, 298 K.

References: **1.** F. Carniato, C. Bisio, R. Psaro, L. Marchese, M. Guidotti, *Angew. Chem. Int. Ed.*, 2014, **53**, 10095-10098.

WS1 OR18

Strategies for analysis of chemical weapons for forensic and legal prosecution”

Murugiah Muthusamy

Fire & Rescue Training Academy, Malaysia

WS1 OR19

For greater good

Antonio Sergio

New DuPont, Italy, Antonio.sergio@dupont.com

DuPont Personal Protection (www.ipp.dupont.com - www.safespec.dupont.it) uses DuPont's experience as one of the safest companies in the world, its recognized scientific and technological skills, and its knowledge of key markets to offer solutions that protect people, goods, processes and the environment.

DuPont Protection Solutions is the world leader in chemical protection clothing and places safety and quality at the center of its strategy. It combines scientific innovation with the experience gained in the production field to provide a complete range of comfortable and reliable protective garments that offer everyone the possibility of operating with maximum efficiency.

For over 50 years, the success of DuPont Personal Protection has been based both on the unique properties of DuPont™ Tyvek® and its cutting-edge technological skills and on the development of innovations. In the ongoing search for reliability, DuPont Protection Solutions already submits its overalls to over 500 chemicals, and regularly tests them with new substances. These superior performances built the reputation of DuPont™ Tyvek® all over the world, which gained total trust from all users.

At the same time, DuPont Protection Solutions provides customers with access to a technical team and an interactive DuPont ™ SafeSPEC™ website for advice and support in the choice of the most suitable garments for their protection requirements.
DuPont Protection Solutions' commitment to safety also includes a complete assistance service on the technical specifications of the garments and training courses on the correct management of protective clothing to ensure that they are worn under the best safety conditions.

WS1 OR20

Fire security and safety of chemical warehouses

Gianmaria Pio[a], *Luca Marmo*[b], *Enrico Danzi*[b], *Ernesto Salzano*[a]

[a] *Department of Civil, Chemical, Environmental and Materials, Università di Bologna (IT)*
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When warehouse stores large amount of hazardous chemicals, both prevention and mitigation systems are mandatory (1). If any accidental (safety) or malevolent (security) fire is triggered, passive system as fire wall and compartmentation, or active system, as e.g. sprinklers, should operate.

The design of these systems is based on the classification and labelling adopted by GHS alone. Nevertheless, there are several examples of the inadequacy of this classification if ambient conditions are affected by the high temperature of combustion products.

Figure 1 shows the typical sequence of fires in warehouse systems, which starts with the ignition (accidental or as an arson) and develops as massive fire and toxic product dispersion.

This contribution gives some examples and clarify some advancement on this topic for this specific case of SME chemical warehouses, which are often lacking guidelines and knowledge for the prevention and mitigation of fire scenarios

Figure 1. Chemical warehouse fires.

References: 1. Salzano, E., Debernardi, M.L., Riccio, D., Danzi, E., Marmo, L., A Case Study of Multiple Explosions of Chemicals Under Fire Conditions, 12th International Symposium on Hazards, Prevention and Mitigation of Industrial Explosions, Kansas City, USA - August 12-17, 2018.

WS1 - Poster Communications

- **WS1 PO01 -** Tanurima Bhaumik, Jayanta Mandal, Kunal Pal, Parimal Karmakar *"Rhodamine 6G based fluorescent chemosensors for selective detection of Al3+ ion: Effect of substituent and ring strain in enhancing its sensing performance."*
- **WS1 PO02 -** Amrita Saha, Pravat Ghorai, Priyabrata Banerjee *"A Cd(II) Based Coordination Polymer Series: Fascinating Structure and Promising Nitro Aromatic Sensing Property"*
- **WS1 PO03 -** Tapan Kumar Mondal *"Development of smart fluorescence probes for efficient recognition of hazardous species and application as biomarker"*
- **WS1 PO04 -** Arunabha Thakur, Sushil Ranjan Bhatta, Bijan Mondal *"Metal-Coordination Driven Intramolecular Twisting: A Turn-On Fluorescent-Redox Probe for Hg2+ Ion Sensing through the Interaction of Ferrocene Nonbonding Orbital and Dibenzylidenehydrazine*
- **WS1 PO05 -** Roberto Consolo, Matteo Guidotti, Raffaella Soave, Vladimiro Dal Santo, Anna Ferretti, Laura Polito, Claudio Evangelisti, Stefano Econdi *"A European Project for strengthening the chemical and biological waste management in Central Asia countries for improved security and safety risk mitigation"*
- **WS1 PO06 -** Matteo Guidotti, Massimo C. Ranghieri, Stefano Econdi *"Detection, Identification and Monitoring of Chemical Warfare Agents, CWAs: a comparison between on-field and in-lab approach"*
- **WS1 PO07 -** Stefano Econdi, C. Bisio, F. Carniato, G. Gatti, A. M. Katsev, S. L. Safronyuk, M. Guidotti *"Design and optimization of Prussian Blue particles for the decontamination of aqueous media from potentially radioactive caesium"*
- **WS1 PO08 -** Vincenzo Vaiano, Giuseppina Iervolino, Vincenzo Palma *"Removal of organic pollutants from aqueous solutions by dielectric barrier discharge non-thermal plasma reactor"*
- **WS1 PO09 -** Roberto Mugavero, S. Abaimov *"CBRNe Critical Infrastructures and Cyber Security"*
- **WS1 PO10 -** Antonia Lopreside, Maria Maddalena Calabretta, Laura Montali, Xinyi Wan, Baojun Wang, Aldo Roda, Elisa Michelini *"Whole-cell biosensors and cell-free systems: new tools for rapid and sensitive detection of heavy metal and bacterial contamination in water"*
- **WS1 PO11 -** Emilia Paone, Angela Malara, Patrizia Frontera, Lucio Bonaccorsi, Francesco Mauriello *"Exploitation of Coffee Silverskin as sustainable adsorbent material for heavy metals remediation of contaminated water"*
- **WS1 PO12 -** M. Martino, V. Palma, C. Ruocco *"Ceria-coated aluminum foams as promising catalysts for the water gas shift process"*
- **WS1 PO13 -** S. Marchesi, F. Carniato, M. Botta, L. Marchese, M. Guidotti, C. Bisio *"Extraction of Lanthanide Ions from Aqueous Solutions with Synthetic Saponite Clays"*
- **WS1 PO14 -** Simona Cavallini, Beatrice Errico, Federico Benolli *"SYnergy of integrated Sensors and Technologies for urban sEcured environMent (SYSTEM)"*
- **WS1 PO15 -** Simona Cavallini, Federico Benolli *"Strengthening chemical and biological waste management in Central Asia countries for improved security and safety risk mitigation (EU CBRN CoE Project 65 - CABICHEM)"*
- **WS1 PO16 -** Olga Sacco, Wanda Navarra, Vincenzo Vaiano *"N-Doped Semiconductors for Photocatalytic Removal of Organic Pollutants"*

- **WS1 PO17 -** Veronica Caratelli, Giulio Dionisi, Silvia Fillo, Nino D’Amore, Alfredo Sansubrino, Florigio Lista, Fabiana Arduini *“Antibody-free biosensors for on site botulinum neurotoxin detection”*
- **WS1 PO18 -** A. Testolin, V. Pifferi, L. Falciola, C. Ingrosso, M. Corricelli, A. Agostiano, M. Striccoli, M. L. Curri, F. Bettazzi, I. Palchetti *“An Electrochemical Approach to Understand the Enhanced Performances of Gold-Based Hybrid Nanomaterials”*
- **WS1 PO19 -** Elena Lucenti, Elena Cariati, Daniele Marinotto, Andrea Previtali, Stefania Righetto *“Cyclic Triimidazole Derivatives as Potential Sensors of Explosives”*

WS1 PO01

Rhodamine 6G based fluorescent chemosensors for selective detection of Al^{3+} ion: Effect of substituent and ring strain in enhancing its sensing performance

Tanurima Bhaumik[a], *Jayanta Mandal*[a], *Kunal Pal*[b], Parimal Karmakar[b]

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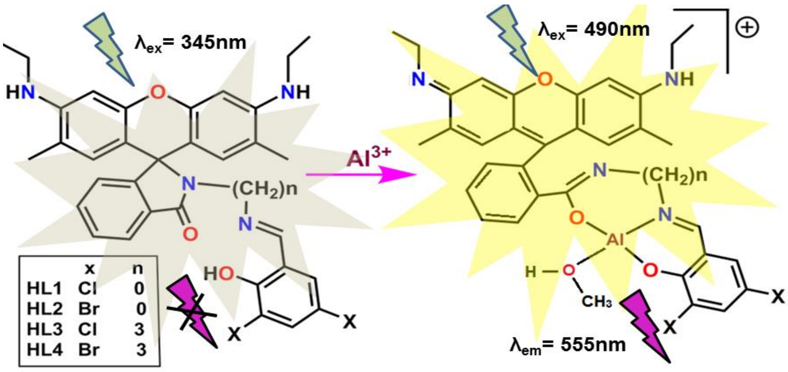
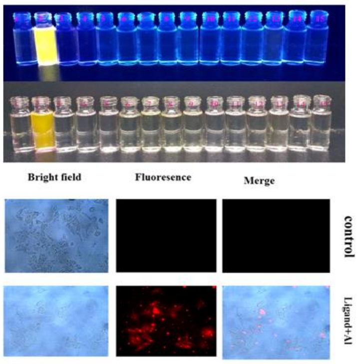
Aluminium is the highest abundant metal in the earth's crust. Materials prepared from aluminum are widely spread in our society. Aluminum toxicity causes Alzheimer's disease, Parkinson's disease, amyotrophic lateral sclerosis, microcytic hypochromic anaemia, osteomalacia, Chemical explosive can be constituted by 2,4,6-trinitrotoluene (TNT) (80%) and Al powder (20%). Preparation of chemosensor for selective detection of Al^{3+} ion is a challenging task owing to its poor coordination ability. Four Rhodamine 6G based chemosensors [HL1-HL4] are designed for selective detection of Al^{3+} ion (1). They are synthesized by condensation between different N-(rhodamine-6G) lactam-diamines and different 3,5- dihalolsalicaldehydes in 1:1 molar ratio in acetonitrile solvent. They are characterized using different spectroscopic techniques and X-ray crystallography. In absorption spectra, chemosensors exhibit intense bands around 530 nm in the presence of Al^{3+}. Presence of Al^{3+} ion turns the colorless solution of the probe to fluorescent pink in visible light. Chemosensors **HL1-HL4** are weakly fluorescent when excited around 490 nm. Presence of Al^{3+} ion enhances emission intensity (555 nm) in many times. It is important to mention that other cations and anions fail to exhibit significant changes in absorption and emission intensities of the chemosensors. Chemosensors are colorless and non fluorescent due to the presence of spirolactam ring. Presence of Al^{3+} ion actuates ring opening resulting pink coloration and high fluorescence. It has been observed that presence of different halogen substituent in the salisaldehyde part and aliphatic spacer in the diamine part of the chemosensors strongly influence their selectivity towards Al^{3+} ion.





References: Mandal, J.; Ghorai, P.; Pal, K.; Karmakar, P.; Saha, A. *Journal of Luminescence* **2019**, 205, 14–22.

WS1 PO02

A Cd(II) Based Coordination Polymer Series: Fascinating Structure and Promising Nitro Aromatic Sensing Property

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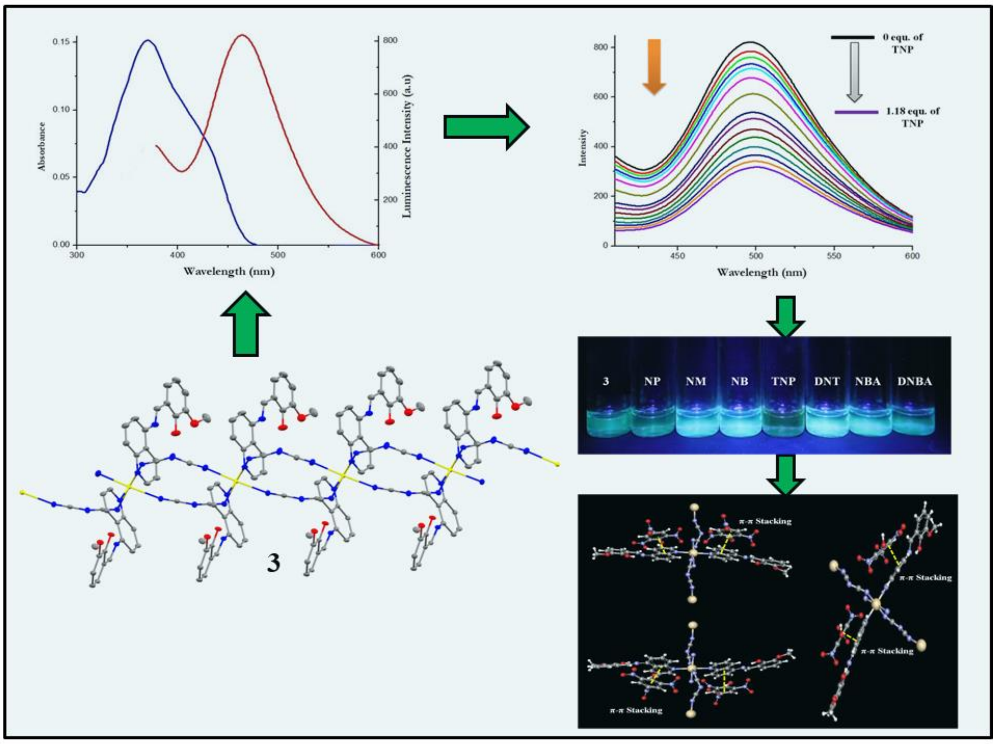
The selective sensitivity of explosive and pollutant nitroaromatic (epNAC) compounds is trending due to their increasing use in terrorist activities, mining and mutagenic properties. (1) Three Cd(II) based coordination polymers (CP) [**1**-**3**] are synthesized and their selective sensing towards 2,4,6-trinitrophenol (TNP**)** are explored. Both **1** and **2** exhibit a yellowish fluorescence at 415 and 416 nm, respectively upon excitation at 360 nm. Luminescence spectrum of **3** exhibits strong visible greenish blue emission at 496 upon excitation at 360 nm. In all three CP emissions intensity is quenched severely in the presence of TNP. It has been observed that binding arrangement of the ligand and co-ligands around the metal centre plays crucial role towards selectivity and sensitivity of TNP. The fluorescence quenching mechanism can be explained by theoretical calculations as RET-ICT based pathways. Mechanism of fluorescence quenching is also highly influenced by structure and coordination arrangement of CPs.



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WS1 PO03

Development of smart fluorescence probes for efficient recognition of hazardous species and application as biomarker

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In recent decades, the fluorescence spectroscopic method has been used vastly to detect various analytes because of its high sensitivity, specificity, easy to operate, low cost and real-time monitoring (1). Detection and imaging of biologically relevant target molecules through fluorescence in living systems has emerged as an area of intense interest in the chemistry-biology interface owing to its significant biomedical implications. These are ideal features for real-time on field measurements, thus the errors caused by the sample transportation and storage can be largely reduced (2). Optical sensors have found many applications in various fields, including biomedical, clinical, and environmental monitoring and process controlling (3,4). All the chemical entities undergo dynamic chemical transformation in the cellular complex environment. Thus bio-inspired emerging strategy for fluorescence based bio-imaging is necessary to sort and identify the reactive species within this complex microenvironment by exploiting differences in molecular reactivity. The main challenge of this is to design such a probe which should be nontoxic, chemo-selective and well co-ordinate to detect short lifetime biological entities within complex biological environment. At the present time more attention has been paid to develop molecular probes to detect various reactive species such as reactive oxygen species and organophosphorus nerve agents etc.. The nerve agents are a class of chemically active and highly toxic volatile liquids or gases derived from organophosphates which are considered to be one of the most poisonous chemicals to human beings as well as to any other human beings. Because of the massive threats offered by the nerve agents in our environment, there is an utmost need of developing a reliable, facile and rapid method of detecting them distinctly.

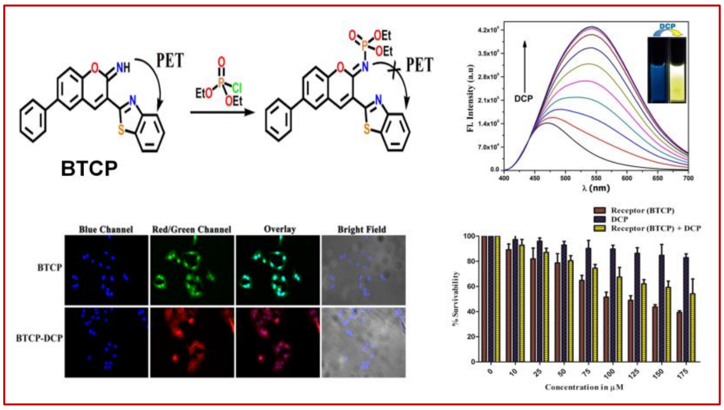

Fig. 1. Detection of organophosphorus nerve agent mimic (DCP) and live cell imaging

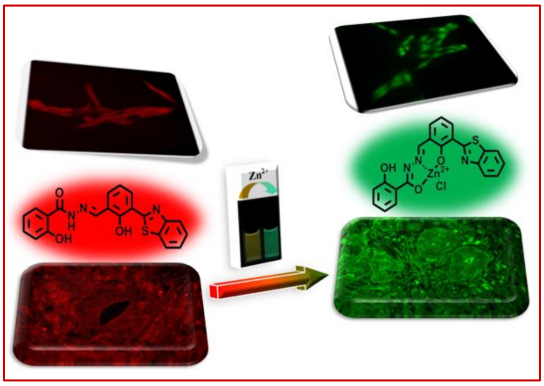

Fig. 2. Detection of Zn^{2+} in cells and tissues

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WS1 PO04

Metal-Coordination Driven Intramolecular Twisting: A Turn-On Fluorescent-Redox Probe for Hg^{2+} Ion Sensing through the Interaction of Ferrocene Nonbonding Orbital and Dibenzylidenehydrazine

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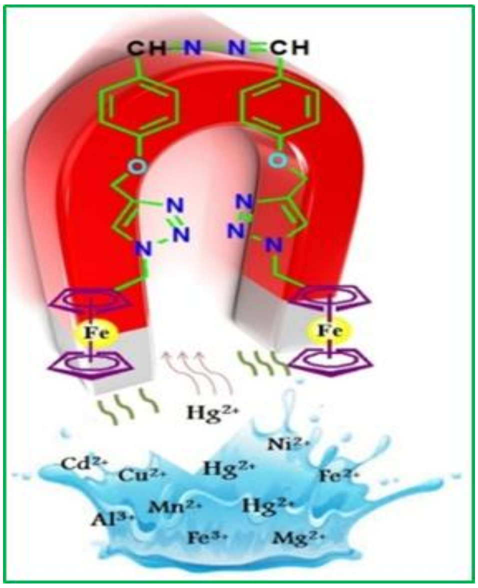
A unique C2 symmetric azine bridged bi-ferrocenyl receptor (**4**) has been modelled and synthesized. In this work, we are able to synthetically regulate conjugation of the dibenzylidenehydrazine fluorophore unit to unexpectedly reveal metal-coordination driven intramolecular twisting. The present probe shows a dramatic turn-on fluorescence response with 91 fold increment of quantum yield along with17 nm blue shift upon binding with Hg^{2+} ion selectively with a limit of detection as low as 15 nM. Upon Hg^{2+} recognition, the ferrocene/ferrocinium redox peak was anodically shifted by $\Delta E_{1/2}$= 78 mV, indicating the formation of a new complex species. The plausible binding mode of Hg^{2+} ion with the compound **4** has been proposed based on ^{1}H NMR titration, high-resolution mass spectrometry (HRMS) study and a density functional theory (DFT) study along with the Job's plot analysis. Interestingly, DFT calculations has revealed that reason for fluorescence enhancement after coordination to Hg^{2+} ion is not due to conventional restricted C=N isomerization or interrupted N-N single bond rotation rather its due to increase of $\pi \leftarrow \pi^*$ transition at the expense of $n \rightarrow \pi^*$ (aromatic) transition of the free ligand. Further, TD-DFT calculations of first excited singlet state of **4** and [**4**·Hg^{2+}] revealed the involvement of the aromatic π electrons with the vacant site of Hg^{2+} ion which may be further attributed to the fluorescence enhancement phenomenon. In addition, the receptor **4** was successfully applied for the detection of Hg^{2+} ion in real samples.



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WS1 PO05

A European Project for strengthening the chemical and biological waste management in Central Asia countries for improved security and safety risk mitigation

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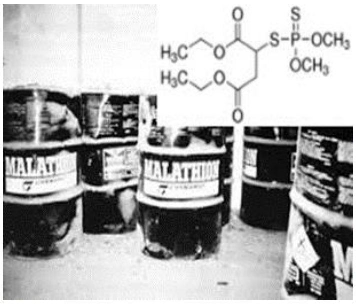
The European Union (EU) CBRN Risk Mitigation Centres of Excellence (CBRN CoE) Project 65 is a EU funded project, which aims at addressing chemical and biological waste management issues in the Central Asia (CA) region, namely in Afghanistan, Kyrgyzstan, Mongolia, Pakistan, and Uzbekistan. The project consortium is composed by five agencies, both public institutions and foundations from Poland and Italy. CNR-ISTM is the leading organization of one working package, whose main purposes are:

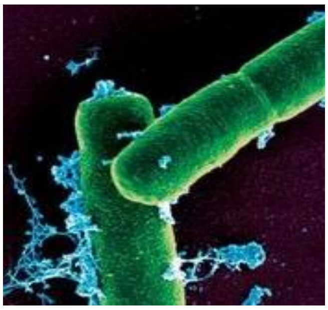
- To raise or enhance the awareness of beneficiary Countries on the correct management of chemical (C) and biological (B) wastes
- To design, plan and organise training sessions on safety & security aspects related to the generation, handling, transportation, containment and disposal of C and B waste materials at different level, *i.e.* from laboratory scale, to minor and major production sites.

These activities will aim at strengthening a local capability to foresee, prevent, minimize and/or mitigate chemical or biological incidents, emergencies and criminal uses involving hazardous materials at both national and regional level. In the first year of activity, a careful analysis and survey on the current scenario in the five countries evidenced some points of concern (1). The most critical situations can be linked to: the presence of hazardous chemical and biological substances in municipal waste, electronic waste containing PCBs (polychlorinated biphenyls) or heavy metals (Pb, Cd), hazardous by-products from mining (cyanides, mercury, metal sulphides and inorganic acids), possible release of hazardous ashes, dusts, dioxins and furans from unsuitable waste incineration, obsolete agrochemicals and organochlorine pesticides, including POPs (persistent organic pollutants), often stored in old and inappropriate sites, and the endemic outbreak of *Bacillus anthracis* in some of the Partner Countries. In this panorama, non-negligible risks may come from an accidental exposure of the population to hazardous C & B materials (2). Nevertheless, one strategic goal of the Project is to discourage the illicit and/or malicious use of toxic/polluting/infectious waste hazardous materials as new sources of threat for criminal purposes or in terrorist acts. In strict cooperation with the main national institutional stakeholders and decision-makers, the European implementers of the Project will organize a plan of tailored awareness raising and a set of training courses in each Beneficiary Country in the period 2019-2020.



Sites with obsolete chemicals exist in CA and need proper management

PCBs are still widely used in electronic devices in Central Asia



Bacillus anthracis is pervasive in CA, posing serious health risks

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WS1 PO06

Detection, Identification and Monitoring of Chemical Warfare Agents, CWAs: a comparison between on-field and in-lab approach

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Hazardous chemical warfare agents, CWAs, exploited in criminal acts or in warfare poses a non-negligible threat to the life of professionals and first responders (firefighters, law-enforcement or armed forces, emergency health service, etc.) involved in civil protection and emergency operations (1). Detection, identification and monitoring procedures are the most suitable options in order to prevent exposure and any form of direct contact between the operator and the toxic agent. In addition, not only the recent alleged use of CWA in the war scenario of the Middle East or in targeted attacks in Europe, but also the permanent risk of accidental release of industrial hazardous materials in major incidents have stressed the key role of an early and effective on-site detection of harmful agents (2,3). For this purpose, a prompt and advanced detection capability is crucial to gather information about the risk, to identify the nature and the concentration of the contaminant, to provide a mapping of the hazardous areas and to define the protection and decontamination requirements.

Along with simple, although effective, manual and conventional detection systems, a broad variety of electronic devices and/or automatic hand-held detectors based on advanced physico-chemical techniques, such as mass spectrometry, infrared or Raman spectrophotometry, photoionization or high-performance gas-chromatography, are available on the market and are essential to first responders who may operate in a potentially contaminated and hazardous environment.

The present contribution will outline a critical brief review of the most widely-known systems and tools for the on-field use at an incident site, with a special emphasis on light-weight deployable gas-chromatograph mass-spectrometry (on-field GC-MS) instruments, photoionization-based detectors (PID) and ion mobility spectroscopy devices (IMS; either with open loop or closed loop technology).

Advanced portable detector, based on IMS technology for the identification of toxic industrial materials and CWAs

Identification of an unknown sample by hand-held GC-MS apparatus in a potentially hot zone

Military-oriented reconnaissance armoured VBR NBC vehicle equipped with detection and identification instruments for chemical, biological and radiological hazardous agents

The particular features and differences between compact, portable devices and conventional in-lab desktop instruments will be highlighted. A comparison between civil-oriented detectors, for fire brigade, civil protection, emergency medical system units and military-oriented apparatuses will be outlined.

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WS1 PO07

Design and optimization of Prussian Blue particles for the decontamination of aqueous media from potentially radioactive caesium

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In the case of a an unintentional incident or a criminal attack at a site dealing with radiological materials, the possible release of hazardous radionuclides into the environment and the risk of internal radiological contamination of living organisms is a topic attracting a growing attention (major events in Chernobyl, 1986, Goiania, 1987, and Fukushima, 2011) [1]. Iron(III) hexacyanoferrate(II), $Fe_4[Fe(CN)_6]_3$, commonly known as Prussian Blue, PB, is a widely adopted countermeasure for the removal of radioactive contamination due to ^{137}Cs in aqueous media, either in liquid waste effluents or in biological fluids [2].

This report describes how a tailored synthesis strategy can affect the PB physico-chemical properties, aiming to maximize the capability of the PB lattice to capture radioactive species from aqueous media (Fig. 1a). The solids were fully characterized by textural, spectroscopic (XRD, FT-IR, DLS) and microscopic (SEM, HR-TEM) techniques. In particular, the specific surface area, pore volume and particle size of the PB samples (Fig. 1b) were tuned to improve their removal properties in pure aqueous media as well as in enteric fluid.

The decontamination capability was measured in the removal of non-radioactive $^{133}Cs(I)$ species from a simulated enteric fluid (500 ppm) and compared, under the same conditions, to a benchmark commercial decontamination PB sample (Fig. 1c). After the 1 h of activity, the tailored PB material removed 85% of the initial Cs content with respect to 63% for the reference sample. This result is remarkably better than the current state of the art.

The toxicological acute and chronic effects of the PB samples were evaluated by means of bioluminescence inhibition tests performed over two strains of luminescent bacteria isolated from Black and Azov Seas (*Vibrio fischeri* F1 and *Photobacterium leiognathi* Sh1) [3]. Notwithstanding the noteworthy difference in physico-chemical properties, the toxicological impact of the two PB samples on bacterial luminescence was modest and similar. Indeed, the solids exhibited only a weak luminescence inhibition and even a slight growth at concentrations up to 0.5 mg/ml. Such results confirmed the low, or negligible, ecotoxicity for the PB compounds studied here.

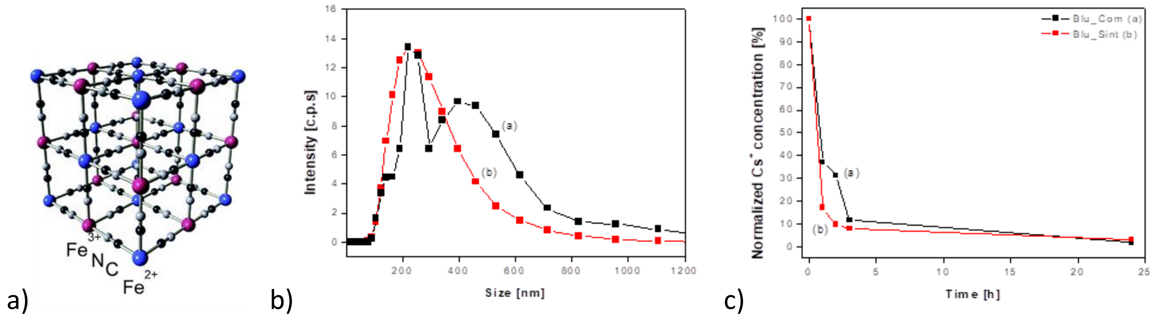

Figure 1. a) lattice structure of PB; b) particle size distribution, from dynamic light scattering analysis; c) $^{133}Cs(I)$ uptake profiles from 500 ppm simulated enteric solution. Red: optimized PB; black: reference PB sample.

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WS1 PO08

Removal of organic pollutants from aqueous solutions by dielectric barrier discharge non-thermal plasma reactor

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In the recent years, a growing interest from the scientific community has been devoted to the technology based on non-thermal plasma (NTP) as possible solution for the treatment of contaminated water.

The interaction of the NTP with water molecules produces many reactive species, such as hydroxyl radicals and ozone with the simultaneous emission of UV light.

In the case of water and wastewater treatment, it would be advisable to select the operating conditions of a process based on a DBD non-thermal plasma reactor able to promote the pollutant degradation and mineralization at very similar rates in order to avoid the formation and the consequent accumulation of reaction intermediates in the treated water.

In this work, the removal of different water pollutants (methylene blue, phenol, caffeine, paracetamol and ceftriaxone) was studied in DBD NTP reactor. The results showed that, using the appropriate selected operating conditions, it is possible to achieve the complete degradation and mineralization of the contaminants with enhanced performances with respect to the available literature about the use of non-thermal plasma technology in water and wastewater treatment. In addition, for each tested pollutant, very similar discoloration and mineralization rates were achieved, suggesting that the pollutant molecules were selectively converted to CO_2 during the treatment time.

WS1 PO09

CBRNe Critical Infrastructures and Cyber Security

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In the era of global communication and increasingly sophisticated technologies, cyber security is gradually becoming one of the major security research areas (alongside with state security, nuclear security, biomedical sciences, etc.), aiming to ensure safety and stability of humanity at the global level.

CBRNe infrastructure, providing enormous benefits and satisfying the daily needs in power and water supply, production of chemicals and their derivatives, biological and medical needs, transportation and military superiority, if not duly secured, can pose existential risks and lead to global cross-border catastrophes. The danger has even more increased with the birth and growth of computer systems and digital communications, which, connecting the world on one hand, at the same time provide covert channels for malicious cyber-attacks enhanced by viruses empowered with Artificial Intelligence. Exponentially growing, dual use Internet-connected technologies are shadowed by elaborated cybercrime tools with the proportionate rate.

Though the CBRNe facilities are duly guarded in the physical world, they remain extremely vulnerable in the cyber reality and attractive to both state and non-state malicious actors. The more sophisticated the target and ramifications are, the more interest they evoke from attackers in need of only one vulnerability to breach the target and the higher protection skills are requested from defenders protecting the systems as a whole.

The current state of the CBRNe Infrastructure is perceived as a global high-risk area in need of enhanced operational cyber security. The advanced persistent threat (APT), the most sophisticated and dangerous type of cyber-attacks, can covertly bypass the highest security levels, reach most vulnerable systems in critical facilities, cause global environmental damage and mass loss of human lives. Involvement of state actors, accessibility of cyber tools, limited information coverage (classified security measures and proprietary undisclosed knowledge), specific vulnerability management of industrial control systems (ICS), Supervisory Controls and Data Acquisition (SCADA), and outdated protocols aggravate the situation, threatening to delay response time in CBRNe events of global concern.

The presentation concludes that with exponential growth of open source cyber tools and commercially available cyber arms, open source electronic equipment, cyber vulnerability is a growing concern for CBRNe infrastructure in all nations, and concerted civil-military efforts at the national and international levels are needed to address future cyber security challenges.

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WS1 PO10

Whole-cell biosensors and cell-free systems: new tools for rapid and sensitive detection of heavy metal and bacterial contamination in water

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Real time routine monitoring of water for chemical and biological threat agents is one of the major concerns of our society. A rapid response to a terrorist attack, as well as to an accidental release of toxic environmental pollutants, requires the ability to rapidly detect chemical and biological agents so that an early warning can be raised, potential health risks defined, and proper countermeasures are employed. In this field cell-based biosensors have been widely used as they provide useful information (such as bioavailability and general toxicity) and they are suitable for on field application. During the last decade, thanks to the implementation of smartphone and other light detectors, cell-based biosensors have been also integrated into compact analytical devices. However, the scarce robustness of living cells still represents an issue and several immobilization methods have been developed for improving cell's shelf-life and obtain ready-to-use biosensors. More recently, cell-free transcription-translation (TX-TL) systems have been also proposed as an alternative to cell-based biosensors. Conversely to whole-cell biosensors, TX-TL systems do not rely on living cells but rather include the biological machinery and energy source to express a reporter protein as consequence of target activation.

Here, we report a side-by-side investigation of whole-cell and cell-free transcriptional and translational system for heavy metal and bacterial contamination in water.

A comprehensive profile of diverse optical reporter genes (with fluorescent, colorimetric and bioluminescent detection) has been reported to compare limit of detection (LOD), sensitivity, input/output dynamic ranges and response time. According to our results, NanoLuc luciferase is the best candidate to our purpose, as it shows the lowest LOD (50.0 fM of $HgCl_2$) within the shortest response time (30 min), proving is eligibility as reporter gene for fast and sensitive on field monitoring.

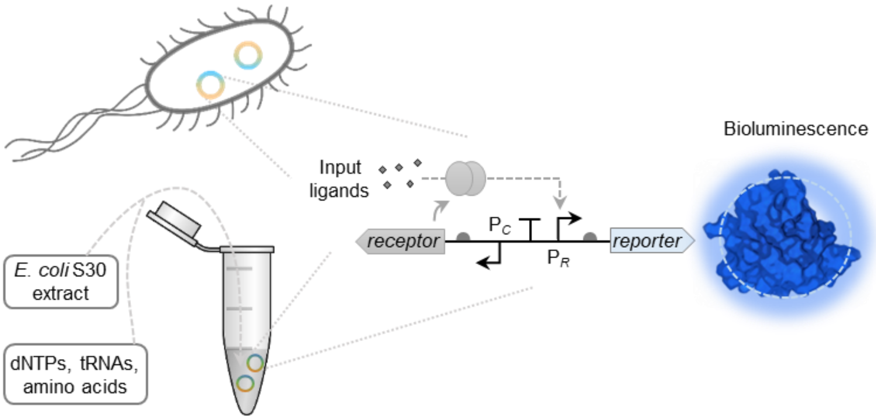

Figure 1. Cell-free vs whole cell reporter gene technology.

WS1 PO11

Exploitation of Coffee Silverskin as sustainable adsorbent material for heavy metals remediation of contaminated water

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In the past few years, in the framework of environmental sustainability research, numerous attempts on the reuse and valorization of coffee byproducts and coffee wastewater have been developed (1). Coffee is the most important food commodity worldwide, being the second-most traded product after oil (2). Because of this extended market, the coffee industry produces huge volumes of waste. In fact, each stage of the coffee production process (i.e., coffee-cherries processing, dried-beans milling, green-coffee-beans roasting), as well as coffee consumption, each year produces a large volume of biowaste, which contributes to environmental pollution (3). Among this biowaste, residues with coffee silverskin (CS) and spent coffee grounds (SCG) are the most significantly produced. In this context, coffee silverskin (CS) has efficiently been used as adsorbent material to remove potential toxic metals (PTMs) as well as heavy metals (HMs).

In order to assess its suitability in water remediation, kinetic adsorption experiments of Copper, Zinc, Nickel, Mercury, Cadmium, Arsenic, Chromium and Lead ions from wastewater were carried out and the adsorption performance of the waste material was compared with that of another well-known waste from coffee industry, spent coffee grounds (SCG) (4).

Equilibrium-adsorption data were analyzed using two different isotherm models (Langmuir and Freundlich), demonstrating that monolayer-type adsorption occurs on both CS and SCG surfaces.

The overall results support the use of coffee silverskin as a new inexpensive adsorbent material for PTMs and HMs from wastewater.

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WS1 PO12

Ceria-coated aluminum foams as promising catalysts for the water gas shift process

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The CO-Water Gas Shift (WGS) operates downstream of the reforming processes; it allows to reduce the percentage of carbon monoxide in the syngas flow to less than 0.3%, increasing the hydrogen yield. WGS is a reversible exothermic reaction, thermodynamically favored at low temperature; the industrial process involves two adiabatic phases, High Temperature Shift (HTS) and Low Temperature Shift (LTS), with an intermediate cooling. The heat of the reaction induces a thermal gradient on the catalytic bed, with a much higher temperature at the outlet of the bed, compared to the inlet, limiting the conversion of CO. To overcome the kinetic and thermodynamic limitations associated with this type of process, the widespread strategy lies in the use of multi-stage processes, which allow the optimal reaction kinetic path to be obtained, with a large number of small steps. This type of configuration is effective but not very efficient, being characterized by high installation and operating costs and the growing need for small-scale plants, in the distributed production of hydrogen as an energy carrier, makes this type of configuration unsuitable and unprofitable. An interesting alternative lies in the use of structured catalysts with high thermal conductivity, which allow the redistribution of the reaction heat along the catalytic bed, with advantages both on conversion and on reaction kinetics (1, 2).

Structured catalysts are usually obtained with washcoating techniques, however this procedure is cumbersome and expensive, furthermore the resulting catalysts are not very resistant to mechanical stresses. The possibility of realizing a resistant coating in a short time, highly active is certainly an attractive topic (3). The chemical conversion coating is currently used as a coating technique for metal surfaces, with the aim of protecting the surface against the corrosion (4). Numerous chemical conversion $CeCl_3$-based baths have been developed, to realize a ceria protective coating on aluminum surfaces. In this paper we present our results on the preparation of structured catalysts obtained by ceria chemical conversion coating on conductive aluminum foams, as structured catalysts for WGS reaction.

Acknowledgements: This work has received funding from the European Union’s Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 734561".

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WS1 PO13

Extraction of Lanthanide Ions from Aqueous Solutions with Synthetic Saponite Clays

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Due to their unique electronic, magnetic, optical and catalytic properties, rare-earth elements (REEs) have been extensively used in the last decades in renewable energy systems and hi-tech products. (1) Thus, the recycling of REEs is of great importance to reduce costs related to their use in the industry and to mitigate the dependence linked to the strategic import of these essential raw materials from remote countries. Traditional processes employed in the recovery of lanthanides are based on solvent extraction, which requires several steps and large amounts of solvents. The development of recovery methods with higher efficiency, lower costs and reduced environmental impact is thus an important challenge. Different solid sorbents based on carbon, porous silica and natural layered materials have been study for this purpose, due to high chemical affinity for *f*-block species.

In this work, we explored two Na^+-exchanged synthetic saponite clays as alternative synthetic solid sorbents for the extraction of lanthanide ions with different ionic radius (La(III), Gd(III) and Lu(III)), from aqueous solutions. Samples are named SAP-20 and SAP-110, the number in the code being the indication of the H_2O/Si ratio used in the synthesis gel. The saponite samples were characterized by different particle size and cation exchange capacity (CEC), equal to 32.6 mmol/100 g and 87.9 mmol/100 g for Na-SAP-110 and Na-SAP-20, respectively. The uptake studies of Gd(III) were performed in pure water, simulated freshwater and seawater solutions, working with different lanthanide concentrations (0.1 and 10 mM). Both solids showed high effective sorption capacity in the first 30 min of contact, followed by a plateau-*like* adsorption up to 5-24 hours. At the end of experiments, Na-SAP-110 extracted an amount of Gd(III) ions (expressed as 'mg of ion per gram of clay') equal to *ca.* 26 mg/g, while Na-SAP-20 captured almost a double amount (*ca.* 49 mg/g), thus indicating a strong relationship between the Gd(III)-uptake and the CEC of clays. The uptake values, indicated in terms of mass-weighted distribution coefficient (K_d)**,** are comparable to the ones of other layered and microporous materials reported in literature, especially for Na-SAP-20 (Figure 1). The same extraction behavior was found for La(III) and Lu(III), with a higher amount of Lu(III) extracted by both saponites. The clays were finally tested in the presence of an equimolar mixture of all the three ions (3.33 mM of each), both in pure water and freshwater, showing a marked selectivity for Lu(III), due to its lower ionic radius.

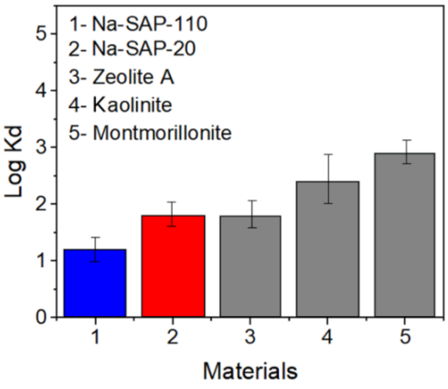

Figure 1. Gd(III)-uptake sorption performance of Na-.SAP-20 and Na-SAP-110 and of reference layered (kaolinite and montmorillonite) and porous materials (commercial LTA zeolite).
Experimental conditions: 15 mg of clay were added to a 1 mL of test solution (pure water, [Gd(III)] = 10 mM), at 298 K.

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WS1 PO14

SYnergy of integrated Sensors and Technologies for urban sEcured environMent (SYSTEM)

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Horizon 2020 is the funding programme implementing the Innovation Union, a Europe 2020 flagship initiative aiming at securing Europe's global competitiveness through the development of breakthroughs and innovative ideas that are the final result of a synergy between research and innovation in a set of domains including security. Among the topics included in the 2016-2017 Work Programme "Secure societies – Protecting freedom and security of Europe and its citizens", SEC-10-FCT-2017 - "integration of detection capabilities and data fusion with utility providers' networks" aimed at supporting project ideas dealing with innovative approaches to be used to detect hazardous substances putting the security of people at risk. Such approaches might involve the placement of a tailored network of sensing devices providing data about the detection of hazardous substances to be integrated through a monitoring centre. "SYnergy of integrated Sensors and Technologies for urban sEcured environMent" (SYSTEM) is the three-year Innovation Action awarded to a consortium led by Fondazione FORMIT addressing the challenge of the SEC-10-FCT-2017 topic. SYSTEM started on 1 September 2018 and aims at developing and testing a customised sensing system for hazardous substances detection in complementary utility networks and public spaces. The proposed innovative monitoring and observing of fused data sources will be tested and eventually adapted in seven urban areas, while carefully tracking Ethics and Legal aspects as well as managing confidential information. To achieve these aims, a wide set of skills and capabilities has been considered key to success, determining the large partnership working on the project, made by 22 partners cooperating with more than ten stakeholders supporting the project activities. Among the project partners, small-medium enterprises developing sensors, universities and research organisations working in the security domain, law enforcement agencies, municipalities, utility network operators, as well as IT industrial partners representing Belgium, Germany, Italy, Poland, Slovak Republic, Sweden, and the United Kingdom will benefit from the ethics and legal expertise provided within the consortium.

Additionally, in order for the project to be successful on the long term, SYSTEM will be developed with the objective to ensure a positive outcome that will be beneficial for improving security of the whole European community through the enhancement of transnational cooperation. This may result in a project replicability, adaptability and/or scalability involving other stakeholders and responding to their specific needs and criticalities.

WS1 PO15

Strengthening chemical and biological waste management in Central Asia countries for improved security and safety risk mitigation (EU CBRN CoE Project 65 - CABICHEM)

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The European Union Chemical Biological Radiological and Nuclear Risk Mitigation Centres of Excellence (EU CBRN CoE) is an Initiative implemented by the European Commission, in cooperation with the European External Action Service (EEAS) and with the support of the UN (UNICRI) and other International Bodies with the aim of strengthening the institutional capacity of non-EU countries to mitigate CBRN risks. The Centre of Excellence includes eight regions which cooperate to strengthen regional capacity in CBRN risk mitigation by increasing local expertise and promoting long-term sustainability actions. Working with Partner Countries, the Initiative encourages local development and enhancement of CBRN action plans, policies and project proposals.

Against this backdrop, the EU CBRN CoE Project 65 *"Strengthening chemical and biological waste management in Central Asia countries for improved security and safety risk mitigation"* - CABICHEM is a three-year project funded by the European Union through the CoE Initiative and implemented to benefit the partner countries of the Central Asia region, namely the Islamic Republic of Afghanistan, the Kyrgyz Republic, Mongolia, the Islamic Republic of Pakistan, and the Republic of Uzbekistan.

CABICHEM started on 1 January 2018 and aims at strengthening existing chemical and biological waste management capabilities to ensure safe and secure collection, transportation, processing, storage, disposal and inventory of hazardous chemical and biological waste originated by local industry, trade, agriculture, health care and past practices (e.g. dumping sites, historical industrial sites, former military bases), as well as due to emergency circumstances.

More in detail, CABICHEM seeks to support national and regional bodies involved in the chemical and biological waste management as well as to assist countries in reviewing and evaluating their legislative provisions on the matter. The project aims further to raise awareness of the issues associated with chemical and biological waste management as well as to provide training activities, including the train-the-trainer approach also based on a tailored e-learning instrument. Site visits and innovative methods for detecting and mapping "hot spots" (satellite remote sensing techniques) enhance the CABICHEM effectiveness towards the implementation of a feasibility study on possible remediation/management of problematic sites to evaluate their practical implementation.

The CABICHEM project is implemented by a consortium of European organisations coordinated by Military Institute of Chemistry and Radiometry – MICHR from Poland and composed by the Military Institute of Hygiene & Epidemiology – MIHE from Poland, Fondazione FORMIT, the Istituto di Scienze e Tecnologie Molecolari – ISTM-CNR and the Fondazione Alessandro Volta – FAV from Italy. To further provide additional effectiveness to the implemented activities national senior experts from each Partner Country with experience in specific CBRN aspects support the CABICHEM partners.

WS1 PO16

N-Doped Semiconductors for Photocatalytic Removal of Organic Pollutants

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As a consequence of the rapid growth of population in urban areas, water use and reuse has become a major concern, leading to an urgent imperative to develop effective and affordable technologies for wastewater treatment. Traditional methods for wastewater treatment are usually based on physical and biological processes but unfortunately, some organic pollutants, classified as bio-recalcitrant, are not biodegradable. In this way heterogeneous photocatalysis may become an interesting water treatment technology to remove organic pollutants not treatable by conventional technique. Photocatalysis, also called the "green" technology, represents one of the main challenges in the field of treatment and decontamination of water and air because it is able to work at ambient temperature and atmospheric pressure. Heterogeneous photocatalysis is a catalytic process that uses the energy associated to a light source to activate a catalyst with semiconducting proprieties. The most common used photocatalyst are TiO_2 and ZnO (1). It is able to oxidize a wide range of toxic organic compounds into harmless compounds such as CO_2 and H_2O. Due to the value of their band-gap energy, about 3.2 eV, they are effective only under irradiation of UV light (2). This is a technological limitation when aiming at implementation of large scale sustainable “green” technologies with renewable energy sources such as solar light. The main research objective is the increase the photocatalytic performances of TiO_2 and ZnO through the doping of their crystalline structure with non-metal ions (nitrogen) that reduce the band-gap making possible the fruitful absorption of the visible light. The synthetized doped samples were characterized by XRD analysis, BET, Raman and UV-Vis spectroscopy. Finally the photocatalytic performances of the doped samples in the removal of model organic pollutants were analyzed and compared.

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WS1 PO17

Antibody-free biosensors for on site botulinum neurotoxin detection

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Botulism is a potentially fatal disease caused by accidental or intentional exposure to botulinum neurotoxin (BoNT) which is mainly produced by Clostridium botulinum an anaerobic, Gram-positive, spore-forming bacterial species. C. botulinum is widely spread in the environment, in both soil and water sediments, and its toxin is primarily transferred to humans through contaminated foods or wounds. This neurological disease manifests clinical syndrome of symmetrical cranial nerve palsies that may be followed by descending, symmetric flaccid paralysis of voluntary muscles, which may progress to respiratory compromise and death (1). The botulinum toxin has also potential use as a biological warfare agent (2).

Given the rapid onset of disease symptoms, it is of great importance to offer a rapid screening instrument to improve food safety and medical diagnosis.

Unfortunately, diagnosis of botulism often relies on the mouse lethality assay or ELISA tests, which require a turnaround time of 2-5 days (3).

Herein, we propose preliminary results of two antibody-free alternatives for the detection of the botulinum neurotoxin, which allow a more rapid diagnosis.

The first one is based on the development of the first paper-based aptasensor for BoNT/A. The BoNT/A aptamer is immobilized on gold nanoparticles modified-electrode thanks to the formation of disulfide bond between the AuNPs and the thiol-oligonucleotide scaffold, which is modified with methylene blue molecule, the electroactive species. The detection of the toxin is carried out by a signal-off method: when the probe-target binding occurs, the distance of methylene blue increased in relation to the electrode surface resulting in a decreased reported electrical signal. The second one is based on the development of a miniaturised sensor based on the proteolytic function of BoNT, which can degrade components of the soluble N-ethylmaleimide-sensitive-factor attachment protein receptor (SNARE) and subsequently cause muscle paralysis (4). For the detection, we used SNAPtide a short peptide which mimics the synaptosomal-associated protein 25 (SNAP-25, a component of the trans-SNARE complex) with a cleavable site.

Acknowledgement

The authors acknowledge the Italian Ministry of Defence for funding (project BIAPTABONT).

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WS1 PO18

An Electrochemical Approach to Understand the Enhanced Performances of Gold-Based Hybrid Nanomaterials

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The interest in hybrid nanocomposites has seen a huge increment over the last decades, thanks to their unique and novel characteristics. These materials can be named as “brave new materials”, with physico-chemical properties that are different and often enhanced with respect to the ones of the relative single components. This is due to the formation of the so-called “heterojunctions”, which are the interface area between the components in intimate contact. Even if the hybrid nanocomposites are widely involved in a plethora of applications (from catalysis to sensing), the understanding of the phenomena occurring at the interfaces are still to be clarified in depth. To fulfil this gap, in this work, we have comprehensively investigated hybrid nanocomposites based on pyrene functionalized Reduced Graphene Oxide (RGO) sheets, surface decorated by organic-coated Au NPs, via Cyclic Voltammetry and Electrochemical Impedance Spectroscopy, along with UV-Vis absorption spectroscopy, TEM and SEM. The RGO sheets are surface functionalized by π-π interactions with 1-aminopyrene and 1-pyrene carboxylic acid; the amino and carboxyl groups provide heteronucleation and growth sites of respectively organic ligand-coated Au NPs (1), of different dimensions (from 3 to 20 nm), which are *in situ* synthesized onto the RGO sheets by colloidal chemical routes. The achieved hybrid nanocomposites have been tested for the electrochemical detection of both organic (dopamine) and inorganic (As) molecules.

We have focus on the role played by every single component of the nanocomposite on the final properties of the sensor device. From these studies, it is evident that the performances of the device drastically depend on the size of the NPs, on the chemistry and length of the ligand capping the NPs surface and on the preparation procedure of the electrode used for the analysis. The results are very promising, since the estimated LODs are comparable or even better than those reported for analogous hybrid materials (2-3). The achieved hybrid nanocomposites are suited for speciate between the two As(III) and As(V) species, and preliminary tests on H_2O_2 detection open the venue to the application of these materials in biosensors. The properties of the hybrid nanocomposites, enhanced with respect to those of the single components, are ascribed to charge transfers occurring at the heterojunction interface between the Au NPs and the RGO sheets, which are assisted and channelled by the pyrene linker.

The obtained promising results moved our attention to other gold-based hybrid systems, which could be conveniently applied in catalysis, electrocatalysis and electroanalytical sensors, also for the detection of emerging contaminants.

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WS1 PO19

Cyclic Triimidazole Derivatives as Potential Sensors of Explosives

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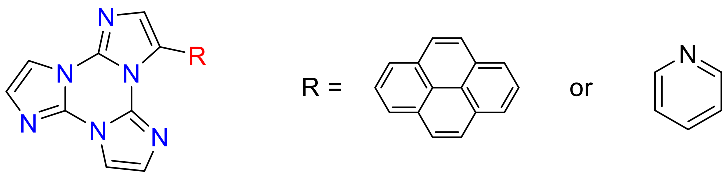
There is an ever growing need for the realization of cheap, portable and simply to use devices for the detection of explosives, which constitute a potential threat both for homeland security and the environment due to their pollution hazard. In the search of low-cost and user friendly detectors, the development of fluorescent sensors has emerged as a promising strategy thanks to the high sensitivity and selectivity of this method (1). Among the wide range of fluorescent materials comprising conjugated polymers, small fluorophores and supramolecular systems, the development of new systems based on the Aggregation Induced Emission (AIE) mechanism has recently proved to be a valuable route thanks to the higher sensitivity of AIE-active materials over non-AIE based fluorescence sensors (2-3). Typically AIE molecules exhibit poor fluorescence in solution while display a significant enhancement of their emission in the aggregate state, often induced by addition of a non-solvent.

On this regard we recently reported a simple purely organic molecule, namely cyclic triimidazole ($C_9H_6N_6$, **TT**) which is hardly emissive in solution but displays crystallization induced emission (CIE, $\Phi = 30\%$ as crystalline powders), due to concomitant fluorescence and ultralong phosphorescence (τ up to 1 s at room temperature), a behavior that has been attributed to the formation of H aggregates (4).

Here we present some novel **TT** derivatives functionalized with chromophores such as pyrene or pyridines which have been preliminary tested as potential explosives detectors. The photophysical properties of the compounds have been investigated in water-THF solutions to induce formation of nanoaggregates which have been exposed to picric acid.



TT

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WS2 – CHEMISTRY MEETS BIOECONOMY

The workshop wants to present and discuss, with an interdisciplinary approach, the contribution of Chemistry to various aspects related to the bioeconomy, evidencing the need for research projects and activities that support a sustainable technological and industrial innovation based on renewable resources for the production of consumer goods. The workshop includes: a) From crop protection and food production to valorisation of food and biomasses wastes; b) Chemistry, reuse and new economy; c) Chemistry, Biomasses and Waste valorisation; d) Expanding Chemistry using Biotechnologies

WS2 - Organizing Committee and Conveners

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- Lucia Gardossi - Biotechnology Interdivisional Group
- Cristina Nativi - Chemistry of Carbohydrates Interdivisional Group
- Oreste Piccolo - Green and Sustainable Chemistry Interdivisional Group

WS2 - Keynote Lectures

- **WS2 KN01** – James H. Clark, University of York, *“Towards a Circular Bio-Economy using Green Chemistry”*
- **WS2 KN02** – Tiziana Milizia, Novamont, *“From Novamont Group a virtuous example of regeneration of deindustrialised sites: Mater-Biopolymer, the highly efficient continuous plant for Origo-Bi biopolyesters production”*
- **WS2 KN03** – Mario Malinconico, CNR IPCB, *“Cellulose, lignin and friends: Waste side stories”*
- **WS2 KN04** – Carlotta Gobbi, Valerio Borzatta, Endura, *“Controlled release formulations with reduced environmental impact”*
- **WS2 KN05** – Lisa Vaccari, Elettra Sincrotrone Trieste, *“FTIR microscopy, tomography and nanoscopy for advanced morpho-chemical characterization of renewable materials using state-of-the art IR sources”*
- **WS2 KN06** – Piergiuseppe Morone, Unitelma Sapienza, *“Change We Can Make: the role of society in the transition towards a circular bioeconomy”*
- **WS2 KN07** – Fabio Fava, Università di Bologna, *“Integrated biowaste exploitation in the frame of circular Bioeconomy: state of the art and opportunities offered by Horizon2020 and the PPP Biobased industry”*

WS2 KN01

Towards a Circular Bio-Economy using Green Chemistry

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Increasing demand for consumer goods from an increasing world population is placing enormous strain on the resources needed by the worlds manufacturing industries. Traditional mineral-derived resources have often been from non-renewable sources located in relatively accessible regions, but these are finite, their exploitation non-sustainable and in some cases they are becoming scarce. At the same time, the wastes generated in manufacturing and in use of the articles of today's society have been allowed to accumulate in rapidly filling landfill sites or disposed of in other environmentally harmful ways leading to serious pollution problems in the atmosphere, land and seas. Waste valorization is becoming more popular but it is mostly small scale and with low efficiency. The most chemically interesting of the large volume wastes is bio-wastes including forestry and agricultural by-products, and industrial wastes including from paper and pulp and food companies. Current bio-waste valorization is largely limited to anaerobic digestion and composting, however, these renewable resources can form the basis of future bio-refineries that can make a very wide array of chemical, material and energy products. To fully exploit the concept and make it widely useful while maintaining environmental advantage, we need to use *Green Chemistry* to ensure that future processes in, and products from bio-refineries are genuinely green and sustainable (1).

Energy efficient green chemical technologies that can convert waste streams into valuable chemicals include low-temperature microwave processing (2) and benign solvent extraction. These can lead to bio-based platform molecules which in turn can be used to make new green bio-based products including solvents (3) and polymers (4). The integration of thermo-chemical and bio-chemical technologies will also become increasingly important as we seek to increase the efficiency of biomass conversion and develop efficient chemistry on fermentation broths (5).

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WS2 KN02

From Novamont Group a virtuous example of regeneration of deindustrialised sites: Mater-Biopolymer, the highly efficient continuous plant for Origo-Bi biopolyesters production

Tiziana Milizia

Head of Research and Development Bioplastic Area - Novamont

Novamont is an international company, leader in the bioplastics sector and in development of biochemicals and bioproducts, obtained from the integration of chemistry, agriculture and environment.

It promotes a model of bioeconomy as a factor of territorial regeneration, based on three pillars:

•Regeneration of deindustrialised sites, thanks to proprietary technologies first in the world, in order to create "bioeconomy infrastructures", integrated with the territory and interconnected with each other.

•Development of low impact integrated agricultural value chains, through the valorisation of marginal land not in competition with food production, integrated in local areas and connected with the bioeconomy infrastructures.

• Products conceived and designed to provide unique and sustainable solutions for specific environmental and social problems, strictly connected with the quality of water and soil. (1)

Mater–Biopolymer is the Novamont group's company dedicated to the production of Origo-Bi, biodegradable biopolyesters with an increasing content of raw materials of renewable origin, essential component of the process to produce the family of biodegradable and compostable bioplastics known as Mater Bi, with a continuous innovation of their technical and environmental performances.

The conversion of previous PET continuous production plant in a highly efficient one for production of new biopolymers is one of the virtuous examples of regeneration of local areas, continuous innovation and valorisation of pre-existing skills and infrastructures. Moreover, Mater-Biopolymer represents a virtuous case of circular economy, indeed the plant is equipped with a complex system of utilities, which contribute to minimizing costs and scraps, through the recovery and reuse of waste. The plant has a production capacity of 100,000 tonnes per year, employs around 90 employees and works hand in hand with Novamont's Research and Development department for a continuous improvement of the process, and to expand the range of products and applications, starting from the use of more and more renewable and local raw materials.

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WS2 KN03

Cellulose, lignin and friends: Waste side stories

Mario Malinconico

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The world of bio-derived polymers and additives coming from agro-industry residues can strongly benefit from the exploitation of different uses and different processing technologies alternative to melt processing. Gel and waterborne varnishes are promising approaches for crop and food protection. Alginates and carrageenans from seaweeds, pectins from residues of apples, citrus and orange, chitosan from shrimp and crustaceous shells are good examples of underused polymeric materials which, alone or by a proper combination with cellulose waste fibers and lignin, can be used in novel formulations. Dip coating, spray application, wet moldings are some of the technologies which are used to provide low cost rigid or flexible packagings for agriculture and food protection.

WS2 KN04

Controlled release formulations with reduced environmental impact

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Several different methods have been tried to create formulations containing active ingredients for agricultural use with reduced environmental impact. We have focused mainly on the following solutions:

1. Use of synthetic polymers (microencapsulation) to minimize the quantity of active ingredients released into the environment (1,2)
2. Use of natural products as possible carriers or complexants (3,4) for synthetic active ingredients
3. Use of natural carriers and/or complexants in combination with natural active ingredients (5,6)

During the presentation, these points will be discussed while highlighting the pros and cons of the above-mentioned solutions, with particular emphasis on regulatory aspects (7).

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WS2 KN05

FTIR microscopy, tomography and nanoscopy for advanced morpho-chemical characterization of renewable materials using state-of-the art IR sources

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The present contribution aims to highlight the potentialities of IR technologies for the 2D and 3D morpho-chemical characterization of materials endowed with advanced and smart functions. The focus will be given to the vibrational analysis of materials at the mesoscale with micrometric and nanometric lateral resolution, which represents the link between macro functional properties of the materials and their molecular composition.

To this aim, the most advanced vibrational techniques available at the infrared beamline of Elettra Sincrotrone Trieste, SISSI (Synchrotron Infrared Source for Spectroscopy and Imaging), will be emphasized and highlighted through targeted examples of Infrared Synchrotron Radiation (IRSR) microscopy at diffraction limited lateral resolution, scattering-type Scanning Near field Infrared Microscopy (s-SNIM) at sub- diffraction limited lateral resolution, and IR-tomography for 3D chemical imaging.

The presented results will mostly refer to the work carried out within the frame of the Interreg V-A Italia – Austria ITAT1023 "InCIMa" (Intelligent Characterization of Intelligent Materials. Partners: Elettra-Sincrotrone Trieste, Salzburg University of Applied Science and Paris-Lodron University of Salzburg.), that concentrates on the analysis of rigid foam of tannin, a bio-resource from wood by-products having potential applications for green building technology.

WS2 KN06

Change We Can Make: the role of society in the transition towards a circular bioeconomy

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Significant changes are ahead of us: most notably, the world's population is projected to increase by almost one billion people within the next decade and the global middle class is expected to nearly triple by 2030. These trends add pressure to the world economic system and environment: greenhouse gas emissions keep growing at global scale, materials and energy sources are fast approaching their physical limits, and the amount of waste produced under the current system seems to be reaching a new peak. Against this background, a transition from a society heavily based on mass consumption, uncontrolled waste generation, and heavy fossil-fuels exploitation toward one based on resource-efficiency, new production and consumption behaviors, waste reduction, reuse, and valorization, seems a desirable and much-needed feat (1).

This change involves a paradigm shift, which goes beyond technological change – it involves big societal and institutional changes as much as the development of radically new technologies. Indeed, policy efforts across a wide spectrum of policy spheres are of utmost importance to guide and steer such transition along the desired trajectory (2). In the literature on sustainability transitions, this insight is captured in the increasing interest in the concept of policy mixes or policy strategies for promoting transitions to more sustainable models of production and consumption and giving rise, in a long-term perspective, to the beginning of a new long wave of sustained (and sustainable) growth.

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WS2 KN07

Integrated biowaste exploitation in the frame of circular Bioeconomy: state of the art and opportunities offered by Horizon2020 and the PPP Biobased industry.

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Bioeconomy is the economy associated with all sectors producing biomass, i.e., agriculture, livestock, forestry, fisheries and aquaculture, and the sectors processing it, such as, the food industry and the biobased industry. The latter is consisting of the wood processing and the pulp and paper industry and biorefinieries, converting non-food biomass and biowaste in novel or innovative products for the modern pharma, cosmetic, chemical, textile and energy industry. They all together are making in Europe € 2,3 Trillion per year of turnover and 18,0 Million of jobs.

In addition to this, Bioeconomy contributes to the reduction of the dependence of current European industry from fossil fuels, and permits to dispose and valorize biowaste, with the production of bio-based chemicals, materials and fuels, thus preventing their environmental impacts and producing valuable compounds that can return then their natural carbon back to the soil. This is the circularity of Bioeconomy and the clear contribution of Bioecony to the achievement of the standards of resource saving and CO_2 emission reduction recommended for the coming years.

Given the wide economic, environmental and social relevance of Bioeconomy, the European Commission consider it as one of the major strategic areas of innovation for Europe.

Thus, a tailored Bioeconomy strategy was launched in 2012 followed by the allocation of a budget of € 3.8 Billion for sustaining research and innovation in the main pillars of Bioeconomy, e.g., sustainable food security, rural renaissance, bio-based industry and services and blue growth through the Societal Challenge 2 of the 7 years framework Horizon 2020. (https://ec.europa.eu/programmes/horizon2020/en/what-work-programme)

Then, a Public Private Partnership, the “Bio Based Industry joint undertaking (BBI JU)” (http://www.bbi-europe.eu/), running from 2014-2020 with a € 3.7 billion public-private budget (27% from the EU commission and 73% from the private Bio-based Industries Consortium), was launched for complementing the Horizon 2020 efforts, by sustaining knowhow and technology transfer in the broad area of sustainable circular Bioeconomy. The main outcomes and opportunities offered by these initiatives will be presented in the frame of the conference.

WS2 - Oral Communications

- **WS2 OR01** – Alisar Kiwan, Eleonora Torricelli, Chiara Samorì, Daniele Pirini, Paola Galletti, Cristian Torri, *“Polyhydroxyalkanoates from sewage sludge: the B-PLAS proof of concept”*
- **WS2 OR02** – Matteo Francavilla, Marone Mauro, Marasco Paolo, Massimo Monteleone *“Reuse of anaerobic digestion effluent for microalgae biorefinery (RAMBIO Project)”*
- **WS2 OR03** – Achille Monegato, Tommaso Carofiglio, Ketty Costacurta,*“Nano crystalline cellulose (CNC) and its application in paper industry”*
- **WS2 OR04** – Paola Fini, Vito Rizzi, Jennifer Gubitosa, Fabio Romanazzi, Dario Lacalamita, Roberto Romita, José Antonio Gabaldón, María Isabel Fortea Gorbe, Teresa Gómez-Morte, Vicente Manuel Gómez López, Angela Agostiano, Pinalysa Cosma, *“Food and Agricultural wastes as Bioresources: recyclable bio-adsorbents to remove/recover emerging Pollutants from water for industrial applications”*
- **WS2 OR05** – Reuben Carr, Fraser Brown, Philip Weyrauch, Alison Arnold, Magali Roger, Frank Sargent, David Smith, *“Improving the Sustainability of Biobased Manufacturing”*
- **WS2 OR6** – Robert McElroy, Roxana Milescu, James Sherwood, Fergal Byrne, Andrew Hunt, Thomas Farmer, James Clark, *“S4 – Intelligent solvent selection towards greening applications”*
- **WS2 OR07** – *Rita Nasti, Federica Zaccheria, Franco Cavazza, Nicoletta Ravasio, Luisella Verotta, “Silverskin: from waste to a renewable source of bioactive compounds”*
- **WS2 OR08** – Paola Di Donato, Annarita Poli, Roberto Abbamondi, Ilaria Finore, Barbara Nicolaus, *“The waste- based biorefinery for the sustainable production of energy and value-added molecules”*
- **WS2 OR09** – Marco Arlorio, Matteo Bordiga, Jean Daniel Coisson, Fabiano Travaglia, Monica Locatelli, Daniela Barile, *“Recovery of high-value ingredients for functional foods and food supplements from wastes and by-products: prebiotic oligosaccharides as case study”*
- **WS2 OR10**- Alessandro Piccolo Mariavittoria Verrillo, Melania Salzano, Vincenza Cozzolino, Riccardo Spaccini, *“New potential nutraceutical application and chemical characterization of Humic matter extracted from green compost”*

WS2 OR01

Polyhydroxyalkanoates from sewage sludge: the B-PLAS proof of concept

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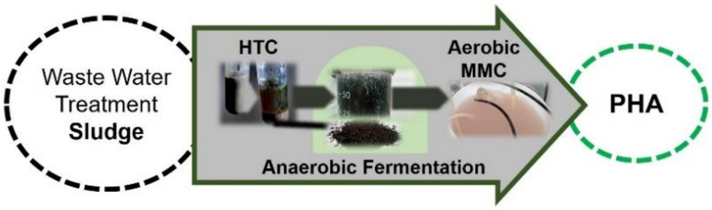
Approximately 40% of chemical energy of food ends up in wastes or in wastewater. Wastewater treatment (WWT) is unequivocally associated to the production of a large amount of sewage sludge, that requires suitable and environmentally accepted management before final disposal. The amount of sewage sludge produced in 2005 by the 27 EU Member States was about 11 Mton of dry matter (1). This material can be subjected to anaerobic digestion (AD), valorizing about one third of its chemical energy and producing a scarcely biodegradable digestate (WWT sludge). WWT sludge is currently disposed of in land (56%), incineration (27%) or landfilling (17%), with greenhouse gas emissions, potential biohazards and variable disposal cost (5 – 120 €/t_{wet}). To date, final disposal strategies neglect the potential use of sludge as feedstock for the production of value-added materials. B-PLAS DEMO project (funded by EIT-climate KIC) aims at exploiting the chemical potential of WWT sludge for producing polyhydroxyalkanoates (PHAs) (Figure 1). PHAs are biodegradable/biocompatible linear polyesters that today cover a niche in the field of bioplastic market (around 2.5% of biopolymers globally produced), mainly because of the non-competitive process costs (5-6 €/kg) if compared with other bio-based/biodegradable plastics (2). B-PLAS DEMO project goal is solving this economical bottleneck by applying an integrated approach in which an initial hydrothermal carbonization (HTC) pre-treatment (150 – 250°C) of WWT sludge is followed by a sequence of biological/chemical processes: i) acidogenic fermentation for converting HTC products into volatile fatty acids (VFA), ii) pertraction of VFA, and iii) aerobic conversion of VFA into polyhydroxyalkanoates (PHAs) through microbial mixed cultures (MMC).

This communication reports the preliminary results of the entire process that will be scaled up to 1 kton/y of PHA in the B-PLAS DEMO project. Among the various HTC conditions tested (temperature and time), a treatment at 200°C for 60 minutes allows to increase by 10 times the soluble chemical oxygen demand (COD) of WWT sludge, allowing to split 44-54% of its COD into an aqueous phase (HTC_{ap}) enriched in small fermentable organic molecules. Acidogenic fermentation of HTC_{ap} converts these substrates into VFA (20% of COD_{HTCap}), subsequently transferred in an aerobic reactor through a trioctylamine-biodiesel liquid membrane in an *ad-hoc* designed pertraction system. MMC convert VFA into PHA (20% of COD_{VFA}). Finally, the extraction of microbial biomass with pressurized dimethyl carbonate (DMC) allowed to produce high quality PHA, with a high molecular weight (0.9 MDa) and a percentage of medium chain monomers (hydroxyvalerate and hydrohexanoate) close to 12%.

Figure 1. B-PLAS DEMO project concept: coupling thermochemical treatments and microbial fermentations to convert C-atoms and chemical energy of wastewater sewage sludge into PHA.



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WS2 OR02

Reuse of anaerobic digestion effluent for microalgae biorefinery (RAMBIO Project)

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In a biorefinery, raw materials do not result from fossils but from biological feedstock. This substitution is an essential step to overcome the fossil dependency and develop low-carbon productive systems. Multiple renewable fuels and a wide spectrum of intermediate materials or end-products are obtained starting from bio-based resources. Consequently, biorefinery is the central concept on which the transition to “bioeconomy” is founded. The challenge of RAMBIO Project was to integrate microalgae production and anaerobic digestion of vegetable feedstocks, agricultural and livestocks wastes applying a “biorefinery” approach. The Anaerobic Digester Effluent (ADE), is the wastewater rich in nutrients produced by anaerobic digestion of organic matter. The use of digestate as non-conventional nutrient source for microalgae growth is particularly interesting for the reduction of the process inputs, coupling microalgae culture and anaerobic digestion. Indeed, the outlet of the anaerobic digesters contains about 50% of the initial nitrogen and phosphorous that can be reused as a source of nutrients and water for microalgae growth, contributing in reducing the production costs. One of the critical aspects for microalgae cultivation is that it requires nutrients in large quantities, which can significantly affect the cost and environmental impact of its production. Applying a life cycle analysis (LCA), it was found that the use of chemical fertilizers for media preparation accounts for 50% of the energy and GHG emissions associated with algae cultivation.

Several reported experiments pointed out the existence of inhibitory effects on microalgal growth, especially with manure wastewater or digestate as substrate. Among the observed effects, high ammonia concentrations and turbidity were often responsible for microalgae growth inhibition. Moreover, contamination of other microorganism can support competition for nutrients reducing biomass productivity of selected microalgal strains, other than precluding the use of cultivated biomass for food and feed application.

In this work, results of RAMBIO project will be discussed. Ozonization of liquid digestate has been used in order to obtain High Quality Digestate ⦃without particulate, turbidity, and microbiological contaminant⦄, to be used as culture medium for microalgae. *Chlorella sorokiniana* and *Scenedesmus bijugatus* have been tested in batch and semi continuous photobioreactors. The produced algal biomass has been tested for a set of biotechnological applications including, fine chemicals and platform compounds extraction (by means of “green technologies”), biodiesel, biooil and biochar production (by thermochemical process).

The innovation of this project was to investigate this integration (so called “biorefinery”) not at laboratory scale, where some studies have already been done, but to work at pilot scale. To the best of our knowledge, no real scale up processes have been carried out. Furthermore, such an integrated approach in academia and industry is still at its infancy and interests in algae-based biorefinery continue to increase because of the necessity to resolve environmental and economic drawbacks of terrestrial biomass-based biorefinery.

The expected results will be the transformation of waste (ADE) produced by agroenergy plants in a high added value biomass (microalgae) that has promising applications in key sectors including energy, biotech, food, pharmaceutic.

Acknowledgement: M. Francavilla gratefully acknowledges the support of APULIA Region - Programma Regionale a sostegno della specializzazione intelligente e della sostenibilità sociale ed ambientale - Intervento “FUTURE IN RESEARCH” – RAMBIO Project: Reuse of Anaerobic Digestion Effluent for Microalgae Biorefinery (Codice Pratica: 8FNCHQ1)

WS2 OR03

Nano crystalline cellulose (CNC) and its application in paper industry

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In the paper world, nanomaterials are already present and widely used. Colloidal materials in aqueous suspensions, such as anionic silicas for retention and styrene/butadiene binders for coating with sizes between 10 and 100 nm, have been used for many years.

Our attention is focused on a material that in the recent years has forcefully appeared in the paper world, and looks promising in many aspects: cellulose nanocrystalline (CNC).

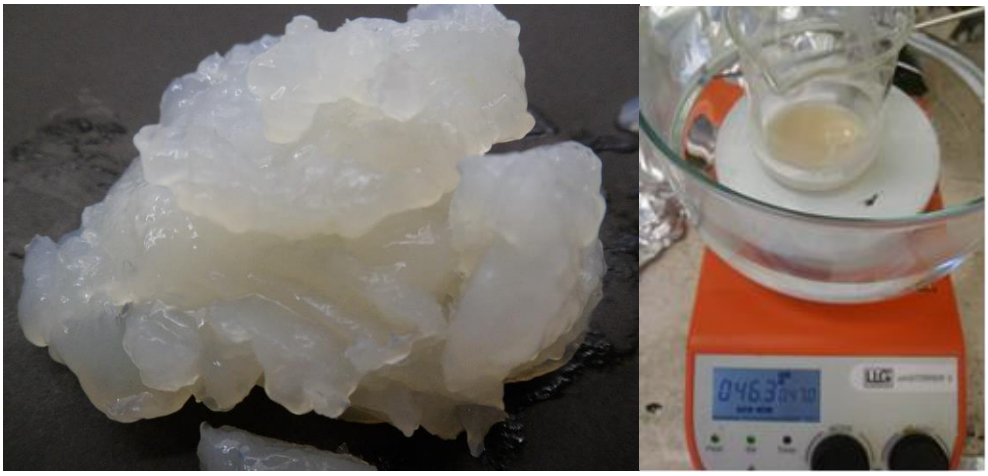
The interest in the CNC is due to the fact that many authors proved that it improves the mechanical characteristics if used in bulk and the barrier properties if it's added on the surface.

These characteristics appreciated in the paper and, in CNC case, would be given by a biodegradable and renewable material.

Several trials have been made:

1. We have synthesized via acid hydrolysis and characterized various CNCs, starting from the standard cellulose used in the paper production (Eucalyptus and NBSK);
2. We have produced laboratory samples through application of the CNC in bulk, on the surface and by printing;
3. We have analysed the obtained paper samples.

In conclusion, in addition to the illustration of the results obtained, considerations of economic nature have been made on the use of CNC in the paper production.



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WS2 OR05

Improving the Sustainability of Biobased Manufacturing

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Ingenza is developing cutting edge biobased manufacturing routes for several industrial end-user chemical company customers. To improve process sustainability and provide a greater choice of feedstock options, Ingenza has been working in collaboration with Newcastle University and Drochaid Research Services on establishing novel proprietary bioprocessing routes.

Through support from Zero Waste Scotland's Circular Economy Investment Fund, our collaboration has demonstrated improved circularity using typical fermentative carbon dioxide off gas that arises during production. The off gas carbon dioxide is recovered and consumed in fermentative preparation of a platform biobased chemical in a two stage bioprocess. Concerted use of renewable power-derived green hydrogen nearly doubles the weight quantity of carbon dioxide that can be assimilated into the biobased product formed compared to using biomass alone as the carbon derived substrate.

This proprietary technology achieves a further stepped improvement in the sustainability profile of biobased chemicals manufacturing to maximise feedstock and energy utilisation whilst also abating biogenic fermentative GHG emission. The demonstration here gives evidence of Ingenza's commitment to deliver cost effective and scalable bioprocesses for the manufacture of chemicals, biologics, pharmaceuticals and biofuels from sustainable sources.

WS2 OR06

S4 – Intelligent solvent selection towards greening applications

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Solvents are a major constituent of chemical processes, and many pose health hazards, safety issues, and can damage the environment. Regulations are clamping down on the use of the most hazardous chemicals, including solvents, most notably REACH. This requires both researchers and industries to look towards solvent substitution and replacement, preferably while also moving towards a circular economy, sustainable model. By applying S4 (Sustainable Solvent Selection Service), we can determine what properties and characteristics a solvent must have in order to be successfully applied to a process, followed by in-silico modeling is applied to create a shortlist of potential solvents. The most feasible candidates can then be evaluated in terms of their hazards, production and availability, and regulatory status and trialed in applications, linking computational predictions with experimental results.

Here I will discuss a number of case studies for materials and reaction chemistries where S4 has been successfully applied and novel chemistries produced.

WS2 OR07

Silverskin: from waste to a renewable source of bioactive compounds

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Silverskin is the thin layer covering the coffee beans. During the roasting coffee process, it is removed becoming a by-product. The large production (150.000 t/year on global scale, of which 7.500 t/years in Italy) of this waste calls for its re-functionalization in order to reduce the impact of industrial by-products in the environment. Currently the only use of coffee silverskin (CS) is as renewable energy source or as fertilizer (1,2), no other utilization has been developed for CS so far. Despite this, the chemical composition of CS indicates the presence of interesting bioactive molecules (*i.e.* lipids, chlorogenics acids, caffeine) that confer to this by-product antioxidant and prebiotic properties. (3) This evidence suggests its re-use as well in other industrial fields such as nutraceutical, cosmetic and pharmaceutical as aimed by *CirCO* project. In this hypothesis of revalorization, it cannot be excluded the potential use of CS lipid matter in cosmetic formulations or as additive for the technology of paper processing (4). For the isolation of CS oil, supercritical CO_2 was selected as more sustainable separation technique, alternative to classical solvent extraction processes.(5) We observed that an appropriate modulation of process parameters (T, P) influence the oil rate and the chemical composition opening the way for targeted extraction. In details the application of mild conditions (35°C, 100/200psi) led to majority extraction of palmitic (C16:0) and linoleic (C18:2) acids with an overall yield of 1.9% ($g_{oil}/100g_{CS}$). The increase of pressure (100 bar→300 bar) and temperature (35°C→60°C) promoted the extraction of arachidic acid (C20:0), behenic acid (C22:0) and lignoceric acid (C24:0) with a calculated oil yield of 3.3% ($g_{oil}/100g_{CS}$). The best identified conditions were employed for the industrial scale-up giving results comparable to laboratory scale. For a possible commercial process application, it is essential to test the applicability of appropriate models for SFE of lipids from oil-containing substrates.(5) For this purpose a mathematical model is constructed based on the experimental data collected, employed apparatus and chemical-physical characteristic of biomass in tightly collaboration with prof. Manenti at Politecnico of Milan.

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WS2 OR08

The waste- based biorefinery for the sustainable production of energy and value-added molecules

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The vegetable waste biomass is produced by several production chains like agriculture, agro- and food industries. Such biomass represents the renewable feedstock for a waste-based biorefinery, an industrial model that plays a key role in a bio-economy system, an innovative economy model that is based on the sustainable use of renewable resources in agriculture and industry, and that takes in account biodiversity and environmental protection (1).

In this frame, the identification of starting materials that are not in competition with food chain or other production chains coupled with the development of new technologies and processes, is one of the main issues for a waste- based biorefinery. Here we reported some examples for the re-use and valorization of two kinds of vegetable waste biomass: the energy crops' residues (2, 3) and the wastes of food industry (4, 5)

The crops selected, i.e. the giant reed (*Arundo donax*) and the cardoon (*Cynara cardunculus*) are among the annual crops and perennial herbaceous species that are object of increasing interest in relation to their use as feedstock for lignocellulose-based biorefinery. The food wastes that have been investigated include the residues of the industrial transformation of tomato, lemon, carrot and fennel, i.e. some most typical cultivation of the Italian agro-industrial sector. These two types of waste biomass have been investigated for their potential as sources of value added molecules and bioenergy.

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WS2 OR09

Recovery of high-value ingredients for functional foods and food supplements from wastes and by-products: prebiotic oligosaccharides as case study

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The isolation, characterization and extraction of bioactive/functional compounds from wastes and by-products from food chains is considered today a strategic aim in modern food science and technology. According with the "circular economy", often correlated to bio-based "green" processes, a large number of by-products are source of very interesting ingredients, addressed both to functional/novel foods and food supplements market. Pigments, antioxidants, fibers, within a potential unique role in nutrition and food technology can be extracted, isolated and – following scale up - processed.

Within the extreme large portfolio of bioactive compounds useful as food ingredients with peculiar characteristics, prebiotic oligosaccharides (PO) from animal and plant sources represent an interesting case study in circular economy. PO from cow whey (oligosaccharides containing fucose and sialic acid, very similar to those contained in human milk) are strategic tools to improve nutritional quality of milk formula or foods for children, modulating the microbiota profile in humans (1). Moreover, a large number of plant-derived oligosaccharides can be easily isolated from wastes and by-products (e.g. perisperm/hulls from roasted seeds; grape seeds; wastes from vegetables processing and other) (2, 3).

This work explores the perspective of isolation, use and formulation of these bioactive compounds, highlighting their capacity to improve in vitro the probiotic growth, also considering and describing new "green" and sustainable technological approaches.

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WS2 OR10

New potential nutraceutical application and chemical characterization of Humic matter extracted from green compost

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A sustainable practice in agriculture is the use of compost as a source of organic matter. In particular, humic substances (HS) and compost tea (CT) extracted from composted vegetable waste are increasingly regarded as efficient biostimulants to improve crop productivity and induce positive responses to biotic and abiotic stress in plants. Moreover, the increasing frequency of antibiotic-resistant infections clearly demonstrates that research of new natural antibiotics is critical for modern medicine. In this context, HS may act as effective carrier of specific pharmacological proprieties such as anti-inflammatory, antioxidant and anti-viral activity and, particularly, in animals may support immune-modulating and anticoagulant effects. A limited literature is currently available on research activities on the antimicrobial activity of humic exctracts; only oxifulvic acids were previously indicated to exert an antimicrobial activity against bacterial strain involved in common human diseases. The impact of HS on human health and the use of these natural products as therapeutic drugs can be an important topic for future research works. The aim of this work was to characterize the molecular composition of HS and CT extracted from different composted biomasses (artichoke, coffee, pepper and citrus) and evaluate their antioxidant proprieties and antimicrobial activities on human common bacterial strains such as Staphylococcus aureus (ATCC 6538P) Pseudomonas Aeruginosa (KK27), Salmonella typhimurium (ATCC14028), Klebsiella pneumoniae (ATCC700603), Enterococcus faecalis (ATCC29212). Artichoke, coffee, pepper and citrus composts were processed in the composting plant at the Castel Volturno experimental farm of the University of Napoli Federico II. Chemical characterizations were carried out by elemental analysis, solid state Nuclear Magnetic Resonance spectroscopy (^{13}C CPMAS NMR), Solution-state ^{1}H NMR spectroscopy, thermochemolysis-Gas Chromatography-Mass Spectrometry (THM-GC-MS) and FTIR–DRIFT Spectroscopy. The antioxidant activity was performed using ABTS method and DPPH assay. Antimicrobial activity proprieties were evaluated by the agar dilution plate viable-count and Minimal Inhibitory Concentration (MIC) method. The molecular characterization performed by ^{13}C-CPMAS-NMR and THAM-GC-MS, showed a prevalence of alkyl, aromatic and carboxyl carbons in coffee-HS, while larger content of methoxyl and phenolic from lignin moieties was found in artichoke-HS. The coffee-CT showed a larger amount of phenolic compounds compared to other CTs. These data have been also confirmed by the Folin-Ciocalteau assay. The results of ABTS and DPPH assay showed that all extracts scavenged the radicals to different extents and showed antioxidant activity, though the highest value was observed for artichoke-HS and coffee-CT. We suggest that the large antioxidant activity of these material may be mainly related to the content of aromatic and phenolic compounds. Furthermore, HS and CT were tested for antimicrobial activity against human common bacterial strains. The HS from artichoke revealed an inhibition of bacterial growth (98%) on all tested strains, while the HS from coffee showed a lower inhibition activity (45%) against Pseudomonas Auruginosa. Coffee-CT revealed a larger inhibition of bacterial growth (58%) thus exhibiting a considerable MIC values (55.5) towards Staphylococcus aureus bacterial strains. These results support the use of compost extracts as promising potential applications in the biomedical field as natural nutraceuticals.

WS2 – Poster Communications

- **WS2 PO01** – Isabella Lancellotti, Luisa Barbieri, Fernanda N. Andreola, Grazia Totaro, Laura Sisti, Maurizio Fiorini, Andrea Saccani *"Residues from Coffee Production and Consume: Formulation of Polymeric and Clayey Materials"*
- **WS2 PO02** – Eleonora Torricelli, Alisar Kiwan, Chiara Samorì, Daniele Pirini, Paola Galletti, Cristian Torri *"B-PLAS DEMO project: Reliable conversion of VFA from fermentation into polyhydroxyalkanoates"*
- **WS2 PO03** – Valeria Pappalardo, Denise Cavuoto, Federica Zaccheria, Nicoletta Ravasio *"Synthesis of biosurfactant by solid acid catalysts"*
- **WS2 PO04 –** Federica Zaccheria, Valeria Pappalardo, Nicola Scotti, Rinaldo Psaro Nicoletta Ravasio, *"Catalytic upgrading of lactose: a rest raw material from the dairy industry"*
- **WS2 PO05 –** Carmine Capacchione, David H. Lamparelli, Alfonso Grassi, Stefano Milione, Francesco Della Monica, Antonio Buonerba, Antonio Proto, Veronica Paradiso *"Toward more sustainable elastomers: stereoregular polymerization and copolymerization of natural linear terpenes"*
- **WS2 PO06 –** Giorgio Tofani, Iris Cornet, Serge Tavernier *"Alternative approach in the filler recovery from recycled paper waste stream"*
- **WS2 PO07 –** Giovanna Speranza, Kalliopi Avramidou, Sara Sangiorgio, Giuseppe Cappelletti, Denise Cavuoto, Nicoletta Ravasio, Teodora Bavaro, Giorgio Marrubini, Daniela Ubiali *"Lipase-catalyzed synthesis of sugar fatty acid esters, a class of non-ionic, bio-based surfactants"*
- **WS2 PO08 –** Giovanna Speranza, Nikolina Vidovic, Sara Sangiorgio, Mattia Cambò, Kalliopi Avramidou, Filippo Fiorentini, Anna Peschiera, Silvia Rapacioli, Teodora Bavaro, Daniela Ubiali *"Enzymatic hydrolysis of protein-rich vegetable matrices. Production and bioactivity evaluation of Hydrolyzed Vegetable Proteins"*
- **WS2 PO09 –** Elisabetta Parodi, Antonella Petri, Oreste Piccolo *"Valorization of low-value products from oil-seed pressing process"*
- **WS2 PO10 –** Reshma Babu, Gustavo Capannelli, Antonio Comite *"Wastewater Biomass Treatment for Their Valorization"*
- **WS2 PO11 –** Tiziana Esposito, Francesca Sansone, Carla Vilela, Nuno H.C.S. Silva, Adelaide Almeida, Annalisa Piccinelli, Rita Patrizia Aquino, Carmen S.R. Freire, Teresa Mencherini *"Design and Development of new packaging films loaded with Chestnut Spiny Burs and Roasted Hazelnut Skins hydroalcoholic extracts"*
- **WS2 PO12 –** Aristide Giuliano, Isabella De Bari *"Technical Assessment of Lignin Valorization Processes"*
- **WS2 PO13 –** Salvatore Impemba, Francesco Della Monica, Carmine Capacchione, Alfonso Grassi, Stefano Milione *"[OSSO]-Type Iron (III) complex for the ring opening polymerization of cyclic esters"*
- **WS2 PO14 –** Mariachiara Spennato, Alice Guarneri Benedetta Rigo, Fioretta Asaro, Cynthia Ebert, Lucia Gardossi *"Biocatalysis for the synthesis and functionalization of renewable polymers and composite materials: taking inspiration from nature"*
- **WS2 PO15 –** Emilia Paone, Maria Michela Dell'Anna, Vito Gallo, Pietro Mastrorilli, Francesco Mauriello, Rosario Pietropaolo *"Transfer hydrogenolysis of lignin and its derived aromatic ethers promoted by the bimetallic Pd/Co catalyst"*

- **WS2 PO16 –** Luca Antoniotti, Gustavo Capannelli, Antonio Comite, Anna Jezowska, Giancarlo Dondo, Simone Stasi, Sara Cepolina *"Pretreatment of waste lignocellulosic biomasses aimed at their chemical valorization"*
- **WS2 PO17 –** Laura Cipolla, Marco Mangiagalli, Beatrice Sciandra, Stefania Brocca, Giacomo Di Foggia, Massimo Beccarello, Marina Lotti *"Enzymatic hydrolysis of lactose to exploit cheese whey as a source of chemical building blocks"*
- **WS2 PO18 –** Cristiano Bolchi, Gianfranco Gilardi, Giovanna Di Nardo, Marco Pallavicini, Claudio Tonin, Marina Zoccola *"FALstaff project: Fatty Acids from Lanolin. Waste wool wax as a source of fatty acids and valuable α-hydroxy fatty acids by integrated biocatalytic and sustainable physico-chemical methods"*
- **WS2 PO19 –** Davide Carraro, Emanuele Amadio, William Denis, Cristiano Zonta, Giulia Licini *"Towards Aerobic Catalytic Biomass Valorization: from simple models to lignin depolymerization"*
- **WS2 PO20 –** Fabrizio Passarini, Mirco Volanti, Nicola Schiaroli, Carlo Lucarelli, Sabrina Copelli, Angelo Vaccari, Benedetta Pellini *"Life cycle assessment of industrial syngas production: comparison between a new steam/dry reforming process and traditional routes"*
- **WS2 PO21 –** Mauro Giorcelli, Mattia Bartoli, Carlo Rosso, Alberto Tagliaferro *"Biochar: a new carbon filler for composite able to improve electrical and mechanical properties"*

WS2 PO01

Residues from Coffee Production and Consume: Formulation of Polymeric and Clayey Materials

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Circular economy is becoming an imperative goal of society in order to ensure further sustainable developments. Agro- residues offer the advantage of being generally non-toxic and can be exploited to recover valuable chemicals such as antioxidant. A different approach takes advantage on the use of agro-residues as fillers to produce polymer matrix composites or as component for ceramic lightweight aggregates for green roofs and agricultural purposes. Coffee is one other important, widespread source of agro-residues, in particular silver skin (SS) is the integument surrounding the coffee beans and after the roasting process, it becomes a by-product. About one hundred kilograms of SS is produced out of five ton of roasted coffee and presently SS is just sent to damping. Moreover, spent coffee ground (SCG), the residue obtained during the brewing process or post-consume product, contains a huge amount of minerals and nutrient substances and became interesting for non-energetic ways of valorization. In the present study, the formulation of both (i) composites containing up to a 30 wt% of SS as a filler exploiting poly(lactic acid) (PLA) and poly(butylene succinate) (PBS) as matrixes and (ii) ceramic lightweight aggregates with up to 20 wt% of SCG as pore forming agent were tested. The lightweight aggregates with 15% wt of SCG were improved using a fertilizer glass (specially designed and containing cattle-bone ash and calcium carbonate) due to its low pH and conductivity values within the soil tolerance range. Results show that it is feasible to produce composite materials by adding SS. This addition is particularly positive in PBS, where a large increase in the Young modulus is obtained. In PLA a trade-off of mechanical properties can be obtained since the value of the Young modulus is increased while the tensile strength is progressively reduced on increasing the filler amount. Lightweight aggregates show excellent porosity of 57.4 % coupled with low bulk density of 1.124 g/cm^3, pH and conductivity in line with the Italian Standard regarding soil amendment (D.lgs. 75/2010), further, nutrients are efficiently released in 21 days (P = 87.73 % and K = 25.74 % of released percentage).

WS2 PO02

B-PLAS DEMO project: Reliable conversion of VFA from fermentation into polyhydroxyalkanoates

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Wastewater treatment (WWT) is unequivocally associated to the production of large amount of sewage sludge, which requires suitable and environmental-friendly management before final disposal. The amount of sewage sludge produced in 2005 by the 27 EU Member States was about 11 Mton of dry matter (1). Nowadays, WWT sludge is currently disposed of in land, incineration and landfilling with variable disposal costs (5 – 120 €/t_{wet}). The idea of B-PLAS DEMO project (funded by EIT-Climate KIC) is to convert sludge from a cost to a benefit: the concept aims at valorizing C-stored inside sewage sludge for the production of polyhydroxyalkanoates (PHA), high added-value biodegradable polymers with a market price between 5 and 6 €/Kg (2). This goal will be reached by developing an integrated approach that couples hydrothermal carbonization (HTC) pre-treatment and microbial fermentations (both anaerobic and aerobic). HTC (150, 200 and 250°C at 15, 30 and 60 min.) increases by 10-times the soluble chemical oxygen demand (COD) of WWT sludge, allowing to split 44-54% of its COD into an aqueous phase (HTCap) enriched in small fermentable organic molecules. Since HTCap at 200°C for 60 min. showed the best COD yields, it was used for anaerobic fermentation tests. Acidogenic fermentation was conducted for 60 days in thermophilic conditions (55°C) in a semi-continuous reactor able to convert 20% of the COD of HTCap into volatile fatty acids (VFA) with an average composition of 62% acetic acid, 28% propionic acid, 4% isobutyric acid, 2% butyric acid, and 4% isovaleric acid. Subsequently, the VFA mixture was transferred in a sequencing batch reactor (SBR) through a trioctylamine-biodiesel liquid membrane in an *ad-hoc* designed pertraction system. A semi-industrial SBR prototype (250 L working volume) was built with standard industrial equipment. This system was inoculated with an activated sludge from a municipal WWT plant and was designed in order to produce 0.1 kg of PHA per day. Mixed microbial culture (MMC) were fed with a mix solution of VFA supplemented with nutrients. During the adaptation period, the length of the SBR cycle was taken at 12 h until significant PHA accumulation was observed. Adapted MMC were then managed changing the cycle length (from 12 to 4 h) in order to maximize dynamically the PHA yield and MMC adaptation. At the beginning of each cycle, 50 L of supplemented VFA solution was added, and 50 L of bacterial slurry was discharged into accumulation reactor (AR, 50 L). Finally, bacteria biomass was collected through filtration and PHA yields, according to different regime of operation, were assessed by low temperature thermolysis (3). The system will be implemented through a dynamic management through a programmable logic controller (PLC) in order to maximize the PHA yield.

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WS2 PO03

Synthesis of biosurfactant by solid acid catalysts

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Sugar fatty acid esters (SFAEs) are amphipilic compounds widely employed as active ingredients in several market sectors for the preparation of food, agricultural, cosmetic and pharmaceutical products thanks to theirs excellent surfactants properties. In fact, depending on the length of carbon chain and nature of the sugar head group, SFAEs cover a wide range of hydrophilic-lipophilic balance (HLB) values. These compounds have many advantages over petrochemical-based surfactants as they are neither harmful to the environment nor skin irritants, food-grade, fully biodegradable and non-toxic. Moreover, some of them showed antimicrobial, anticancer and insecticidal activity (1). SFAEs can be produced from renewable and low-cost agricultural resources by using both chemical and enzymatic esterification. Traditional chemical synthesis of SFAEs requires harsh reaction conditions that result, in most cases, in complex mixtures of esters isomers and by-products. The enzymatic route is a safer alternative but the main drawback is the achievement of sugar monoesters as main products, even if many industrial applications require the use of polyesters. To overcome these limitations, basing on our expertise on solid Lewis acid materials (2), we began to study the activity of clays as heterogeneous acid catalysts, in particular Montmorillonite, a layered aluminosilicate that showed a high activity in the esterification of polyols with long-chain fatty acids (3). Montmorillonite, being environmentally friendly, cheap, thermally stable, and easily easy to handle and recover, can be an alternative strategy to overcome the chemical and enzymatic synthesis limitations.

The synthesis of α-D-glucose-palmitic acid esters was carried out by using four different types of montmorillonite (commercial KSF, K10, K30, and cation-exchanged K10/Fe) in presence of acetylacetone at different temperatures (Figure 1). Two main products were isolated by flash chromatography reaching yield higher than literatura data, especially in presence of the cation-exchanged clay (43% conversion). The esters were fully characterized by NMR and MS analyses.

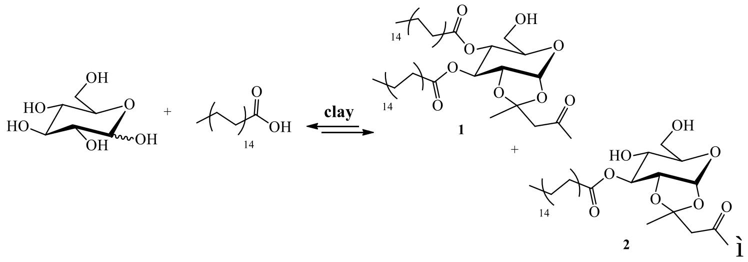

Figure 1

According to Griffin's method (4), the HLB values of products 1 and 2 were 4.8 (water in oil emulsifier) and 7.1 (wetting and spreading agent), respectively. The esters showed interesting interfacial properties, being able to decrease the interfacial tension between sunflower oil and water from 23 to 16 mN m^{-1} in presence of 0.5 w/v % of the partially purified mixture. Each catalyst was characterized by the investigation of the surface area and the type and quantity of acidic sites through FT-IR spectra after pyridine absorption. Results showed that a higher acidity favors the esterification, in particular the conversion increases with the quantity of acid sites.

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WS2 PO04

Catalytic upgrading of lactose: a rest raw material from the dairy industry

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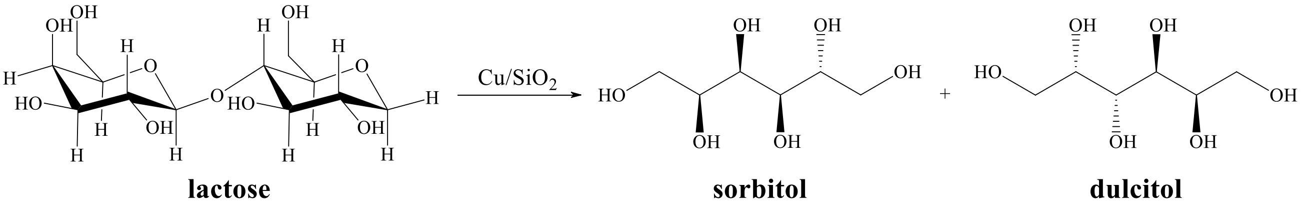
The valorisation of wastes originating from the agro-food industry is a highly strategic way to face the circular economy challenge (1). Among these, milk whey from cheese production is a significant one and the high quantity of lactose derived after protein extraction (e.g. 80 000 tons per year in the plant of Arla in Denmark) pushes to its upgrading into more valuable derivatives, not only as a food ingredient but also as a raw material for the bio-based industry.

The one-pot transformation of lactose into sorbitol and dulcitol has been tested by using two low loading copper catalysts prepared by the chemisorption-hydrolysis technique over different kinds of silica (see Figure and Table).



Cat	T (°C)	Conv %	% reduced sugars
Cu/SiO_2 A	180	100	80
Cu/SiO_2 B	150	72	22
Cu/SiO_2 B	160	96	57
Cu/SiO_2 B	180	100	75

Silica supported copper catalysts gave effectively good results in the one-pot transformation of lactose into a high yield mixture (75–86%) of sorbitol and dulcitol (2). Both conversion and selectivity to reduced alcohols were found to increase with temperature up to 180 °C and the experiments carried out at different temperatures allowed us to shed some light on the reaction mechanism. The process selectivity can be switched to direct hydrogenation of lactose to lactitol only by changing the solvent. The effect of the textural properties of the different silica has been also studied.

This process pave the way to the production of monomers for bioplastics starting from a dairy industry waste. Thus, from sorbitol (usually obtained from food sources) a polymer combining most of the advantageous properties of Polycarbonate (PC) and those of the Polymethacrylate (PMMA) is already produced on an industrial scale.

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WS2 PO05

Toward more sustainable elastomers: stereoregular polymerization and copolymerization of natural linear terpenes

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During the last two decades the emergence of newly industrialized countries with large population such as China, India and Brazil has engendered a tremendous growth of the automotive industry aimed to satisfy the requests of these new markets. This rise has triggered consequentially the increase in tire demand whose production rely on both natural and synthetic rubber.

In particular, in the last years, the production of synthetic rubber greatly exceeded the production of natural rubber because on one hand the cultivation of the rubber tree (*Hevea Brasiliensis*) is circumscribed to few climatic areas of the planet and on the other hand the final properties of synthetic rubber can be better tailored by judicious choice of the reaction parameter (feed composition, catalyst, reaction conditions, etc.).

In this scenario, the search of alternative, bio-based monomers, for the synthesis of synthetic elastomers is highly desirable in order to reduce the consumption of non-renewable resources. Among the compounds derived from biomass, terpenes are a large family of hydrocarbons present mainly in plants and insects with cyclic or linear structure characterized by the presence of conjugated double bonds.

In the last years, terpenes are emerging as viable candidates to serve as building blocks for the synthesis of polymers. In particular the simplest monoterpenes obtained in large scale from turpentine, have been showed to be excellent starting molecules for the synthesis of a wide range of polymers. Namely these compounds can be easy functionalized to give access to a wide variety of polymers: polyketones, polyesters, polyamides, cycloolefinic polymers via controlled/living cationic polymerization or ring opening polymerization (ROP)(1,2).

Furthermore the stereoregular polymerization of linear monoterpenes, derived by pyrolysis from pinenes, myrcene and its isomer β-ocimene has been also reported to be promoted by catalytic systems based on lanthanide (3,4) or iron.

Herein we report the homopolymerization of several linear terpenes and the their copolymerization with butadiene and styrene in the presence of soluble titanium and cobalt complexes activated by methylalumoxane. Copolymers compositions were found to be easy tailorable through opportune variations of the alimentation feed. The polymers obtained were fully characterized through gel permeation chromatography (GPC), differential scanning calorimetry (DSC) and nuclear magnetic resonance (NMR).

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WS2 PO06

Alternative approach in the filler recovery from recycled paper waste stream

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Paper & Pulp industry is one of the main industrial activities in the world. Around 400 million tons of paper and paperboard are globally produced each year (1). In this field, recycling is a fundamental aspect to reduce consumption of virgin fibres from wood and, as a consequence, prevent deforestation. However, used paper products contain several materials in addition to the fibres such as fillers, inks and adhesives (2). From the chemical point of view, these materials are calcium carbonate, kaolin, inorganic pigments such as iron compounds and organic components such as polyvinyl acetate. Paper of newspapers and magazine need the removal of these material because they cause problems in the papermaking and optical properties of the final products. The brightness cannot be realised. The removal of these contaminants is realised through a process called deinking that consists in a flotation to remove the hydrophobics components (contaminants) from the hydrophilic materials (fibres). This process causes the formation of a waste stream defined as “Deinking Sludge”. Around 180 kg of waste is formed to produce 1 ton of newspaper (1). A recovery of that waste is necessary to avoid the use of landfills to get rid of the them. The main method is the incineration of the “Deinking Sludge” at temperature around 900 °C to remove the carbonate and produce oxides (3). The ashes are then used in the building and construction industry.

The target of our study is to propose a different valorisation path of the inorganic components of the “Deinking Sludge” of newspaper and/or magazine production. The calcium carbonate structure can be preserved by incineration at 575 °C of sludge (4). The obtained ashes have a brightness value suitable to be used as filler for newspaper production (ISO brightness >55). In addition, by applying a bleaching step with dithionite, the ashes can be used for magazine production (ISO brightness >66). So, a low-grade waste can be transformed in valuable material. It was also noticed that the brightness of dry ashes did not decrease by time

In the final step of the project, paper sheets were made from recycled pulp of newspaper in presence of bleached ashes from paper sludge and their physical properties were studied. An increase of brightness and opacity was found but with a reduction in terms of porosity and breaking length.

In conclusion, application of this method could be an alternative for the inorganic material recovery and its use as filler. Further studies in terms of process optimization and economic analysis will be necessary for a decision to go for scaling-up.

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WS2 PO07

Lipase-catalyzed synthesis of sugar fatty acid esters, a class of non-ionic, bio-based surfactants

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Surfactants (surface-active agents) are amphiphilic compounds which can reduce surface and interfacial tensions by accumulating at the interface of immiscible fluids. Due to these properties, surfactants alter interfacial behavior and impact on the way other molecules behave at interfaces and in solution. (1) Surfactants constitute an important class of chemicals widely used in almost every sector of industry. However, environmental and health concerns about the effects of the conventional surfactants have increased the demand for surfactants from natural raw materials that possess good biodegradability and low toxicity, along with the desired functional performance.

Sugar fatty acid esters (SFAEs), usually called sugar esters, are non-ionic surfactants which are characterized by excellent emulsifying, stabilizing and detergency properties. Depending on carbon chain length and nature of the sugar head group, together with the many possibilities for linkage between the hydrophilic sugar and the hydrophobic alkyl chain, SFAEs cover a wide range of hydrophilic–lipophilic balance (HLB) values which result in tunable surfactant properties. SFAEs have many advantages over petrochemical-derived surfactants as they are neither harmful to the environment nor skin irritants, are fully biodegradable and non-toxic. More interestingly, they can be produced from renewable resources. (2)

Chemical synthesis of SFAEs requires harsh reaction conditions which result, in most cases, in complex mixtures of monoesters, di- or triester isomers, and by-products. Enzyme-based synthesis is an alternative strategy that can overcome the above mentioned drawbacks: enzymatic reactions occur under milder conditions and do not generally require tedious protection/deprotection steps. Sugar fatty acid esters can be prepared, indeed, through an esterification reaction between a sugar ($C_n(H_2O)_n$) and a fatty acid (RCO_2H) catalyzed by a lipase. (3-5)

In this work, SFAEs, including glucose monooleate (GluMO), monostearate (GluMS), monopalmitate (GluMP), monolaurate (GluML), and galactose monooleate (GaMO), monostearate (GaMS), monopalmitate (GaMP), monolaurate (GaML), were synthesized by enzymatic esterification of fatty acids and the corresponding sugar. Immobilized lipases were used to catalyze this reaction in organic solvent by using molecular sieves (4 Å) to scavenge the water by-product and thus shift the reaction toward sugar ester formation. Reaction yields and product characterization were assessed by ^{1}H NMR.

A rational design of enzymatic reactions was carried out by using the synthesis of GluMP as the model reaction. Sugar:fatty acid ratio, temperature, and reaction time were selected as variables (response: product yield).

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WS2 PO08

Enzymatic hydrolysis of protein-rich vegetable matrices. Production and bioactivity evaluation of Hydrolyzed Vegetable Proteins

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Protein-rich food are a source of bioactive hydrolysates and peptides that have a potential as health-promoting functional foods, dietary supplements and pharmaceutical products. Bioactive peptides are short sequences of amino acids that are inactive within the sequence of the parent protein but can display interesting biological functions once they are released after protein hydrolysis (*i.e.* gastro-intestinal digestion, food processing, microbial fermentation, chemical and/or enzymatic hydrolysis). (1) To date, numerous peptides and hydrolysates with a biological function, such as angiotensin converting enzyme inhibition, mineral binding, antidiabetic, satiating, immunomodulating, opioid, antioxidant, or antimicrobial activities, have been reported. (2,3)

Challenges for production of bioactive peptides include: (i) the development of efficient bioprocesses for peptide production, (ii) the identification and isolation of new molecules, (iii) the elucidation of the mechanisms of action involved in their bioactivities. The lack of economically viable, large-scale purification and characterization techniques is limiting the development of industrial production of bioactive peptides and hydrolysates. (2) Inexpensive protein sources to be used as raw materials and new production and separation technologies are, indeed, being sought.

Starting from the know-how developed over the years in the valorization of protein-rich feedstock such as hemp (3), flax (4), and rice (5), the residue derived from soybean and sunflower seeds was here exploited for the production of protein hydrolysates (HVP, Hydrolyzed Vegetable Proteins).

Enzymatic methods based on proteases are the most common way to produce bioactive peptides. The use of enzymes is preferred to other processes since reproducible molecular weight profiles and peptide composition are usually obtained. Moreover, enzymatic methods are safer and milder than acid hydrolysis. The critical hydrolysis parameters (temperature, pH, aqueous or buffered solution) must be optimized for each protein substrate and each selected enzyme or combination of enzymes.

Enzymatic hydrolysis of soy proteins by food-grade proteases was carried out. Enrichment of peptides contained in HVP mixtures was achieved by using membrane filtration procedures (1÷10 kDa). The resulting HVP fractions are currently under evaluation for their antimicrobial activity.

Upgrading of agro-food residues by enzyme-aided processes (*i.e.* biocatalysis) to obtain high-added value products is a clear example of "circular economy" where waste or by-products are managed sustainably by turning them into a resource, thus contributing to the development of new production pipelines and patterns. (6)

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WS2 PO09

Valorization of low-value products from oil-seed pressing process

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The oil-seed pressing process leads to a significant waste, around 35 million of tons only in the UE and this biowaste is often used for low value applications, such as animal feed or energy production by incenerization (1). The remaining cake from the oil-seed pressing is composed by oils (about 10%) and protein materials. The aim of this research that is included in a PhD thesis work is to give higher value either to the oil-rich part, realizing opportune biocatalyzed transformations, or find new extraction methods for the purification of the protein materials and/or of the corresponding aminoacids constituents for a possible human use. The oil part is rich in triglycerides containing mono- and poly-unsaturated fatty acids, that need to be hydrolyzed to obtain the correspondent fatty acids. They are starting material for the enzymatic production of green notes fragrances and of bifunctional alkyl chains, useful building blocks for bioplastics and biolubrificants, as such or after biocatalyzed manipulations. Thus, in this context, we are preliminary evaluating the possibility to obtain a sustainable protocol for recovering these fatty acids, as well as to separate the protein fraction, from cakes derived from linen, sunflower and camelina sativa industrial oil-seeds pressing. A comparison of the results of the extraction by traditional and deep-eutectic solvents as well as of the biocatalyzed hydrolysis will be presented.

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WS2 PO10

Wastewater Biomass Treatment for Their Valorization

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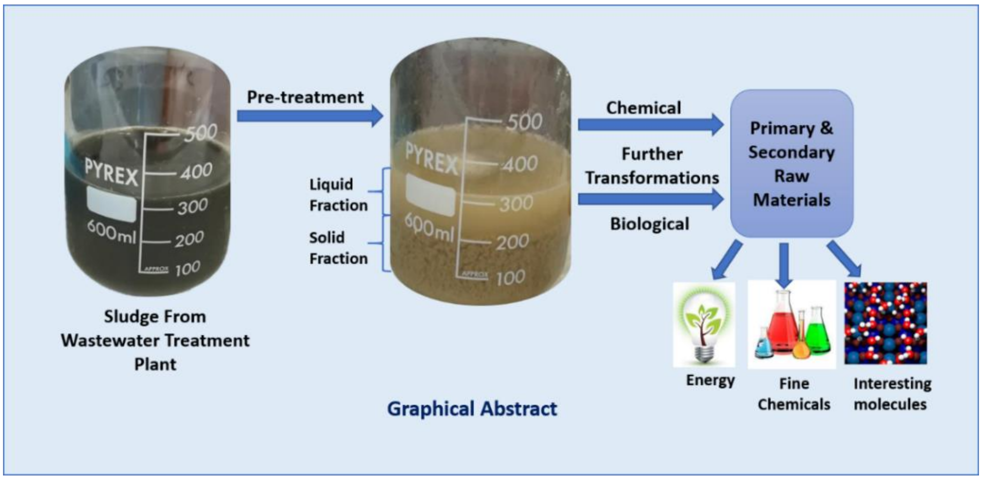
The increasing worldwide energy consumption, higher energy requirements for future, exhaustion of fossil fuel resources and global warming have driven researchers to utilize renewable sources such as biomass to meet energy demands (1, 2). In a vision of Circular Economy, valorisation of secondary biomass and waste can offer a sustainable way to obtain more useful products like fuels and chemicals either directly or indirectly. In this project we aim to valorise the biomass produced from civil and industrial wastewater treatment plants keeping in mind the large quantities of sludge produced annually in Europe. The total wastewater sludge production in terms of dry solids is approximately ten metric tons across the European Union (3). With the increasing number of wastewater treatment plants and the stricter effluent discharge laws enforced on them, the rate of biosolid production is further expected to increase (4, 5). Pre-treatment of the raw biomass is necessary to release the simple molecules and sugars which are enclosed in its complex heterogeneous matrix to make them suitable for further chemical or biological transformations. The objective is to use different pH varied pre-treatment techniques to transform biomass as primary/ secondary raw materials for energy generation or production of interesting molecules and fine chemicals. The pre-treated sludge is separated into solid and liquid fractions and tested for AAS, IC, SEM, TGA, COD. Measurement of total solids, volatile solids, total carbohydrates, hardness, alkalinity and ammonium ions are also done quantitatively. The analysis of the solid and liquid fractions before and after pre-treatment helps to better understand the optimization strategies for the efficient separation of useful molecules from the organic phase. This research project is funded by Regional Operational Program for Liguria-European Social Fund 2014-2020 in co-operation with Ticass Scrl, Iren SpA, Micamo Srl and Active Cells Srl.



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WS2 PO11

Design and Development of new packaging films loaded with Chestnut Spiny Burs and Roasted Hazelnut Skins hydroalcoholic extracts

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Every year the agro-food industry generates large volumes of waste and by-products deriving from the phases of harvesting, processing and production of foods such as fruit and vegetables. Their disposal in landfill generates harmful effects on the environment and public health, but the removal has a negative impact on industry economy (1). Moreover, one of the main challenge of the food industry is to employ renewable and eco-friendly resources as packaging systems, able to replace the petroleum derivatives, also preserving food quality longer (2). For this purpose, the present work focuses on design and development of edible films, by Casting technique, containing extracts obtained from agro-food wastes and by-products, aiming to contribute to the zero waste society and country. Polyphenol-rich extracts from Roasted Hazelnut Skins (RHS-H) (*Corylus avellana* L., Betulaceae family) and Chestnut Spiny Burs (CSB-H) (*Castanea sativa*, Fagaceae family), with proven antioxidant and antimicrobial properties (3; 4), into pullulan-based edible films. Pullulan is a water-soluble, non-toxic biopolymer. It has good abilities in forming transparent, flexible, odourless films with good mechanical properties (5). The challenge of the research was to combine the functional properties of CSB-H and RHS-H with the film-forming ability of pullulan. The effects of CSB-H and RHS-H addition on mechanical properties, thickness, infrared spectroscopy characteristics, and optical properties, were evaluated. The antioxidant and antibacterial activities against Gram-positive and Gram-negative foodborne pathogens, were also investigated. The results showed that the addition of RHS-H and CSB-H reduced the light transmittance of films in the visible and UV ranges, which can contribute to the reduction of food deterioration. The addition of RHS-H and CSB-H did not affect mechanical properties of the films, but was able to confer antioxidant and antimicrobial properties. Findings support the up-cycling of wastes and by-products as a resource of new active ingredients for food purpose. The recycling of agro-food residues reduces the environmental impact also increasing the eco-sustainability of food processing industry, fully matching the main goals of the circular economy.

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WS2 PO12

Technical Assessment of Lignin Valorization Processes

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Lignocellulosic biomass, comprising either herbaceous and woody feedstocks, is currently widely used in many biorefineries. The main biomass constituents are cellulose (30-50 %$_{\text{DRY}}$), hemicellulose (20-30 %$_{\text{DRY}}$), lignin (20-35%$_{\text{DRY}}$) (1). Biomass pretreatment and fractionation can be implemented through different techniques based on chemical, chemical-physical and biological processes (3). The resulting lignin is typically considered a side stream and it is locally used in the cogeneration section of the lignocellulosic biorefineries to produce heat and electricity. However, lignins hold great potential to be used in several industrial sectors to produce bio-based materials and several chemical building blocks. There is a huge research effort to identify the best lignin conversion technologies. Novel technologies allow to obtaining low molecular weight compounds such as aromatic or cyclic compounds till hydrocarbons (5). The main challenge is to develop novel processes able to convert lignin in a selective, efficient and sustainable way to novel and/or drop-in biobased products.

In its Research Centre of Trisaia, ENEA has built technological platform belonging to the national relevant infrastructures which enable the development of various processes from the bench to the pilot scale for the conversion of biomass and its components to value-added products.

In this work, an updated overview of the main processes developed so far is presented. In particular, conversions, energy needs, product value, have been assessed for each process technology as briefly schematized in Figure 1.

Preliminary results show that the base hydrolysis and the reductive conversion of lignin are the most efficient technologies in order to produce the phenolic compounds. While the thermal processes (gasification and pyrolysis) are more advantageous from the energy point of view, but multiple processes are necessary to obtain target value-added bioproducts.

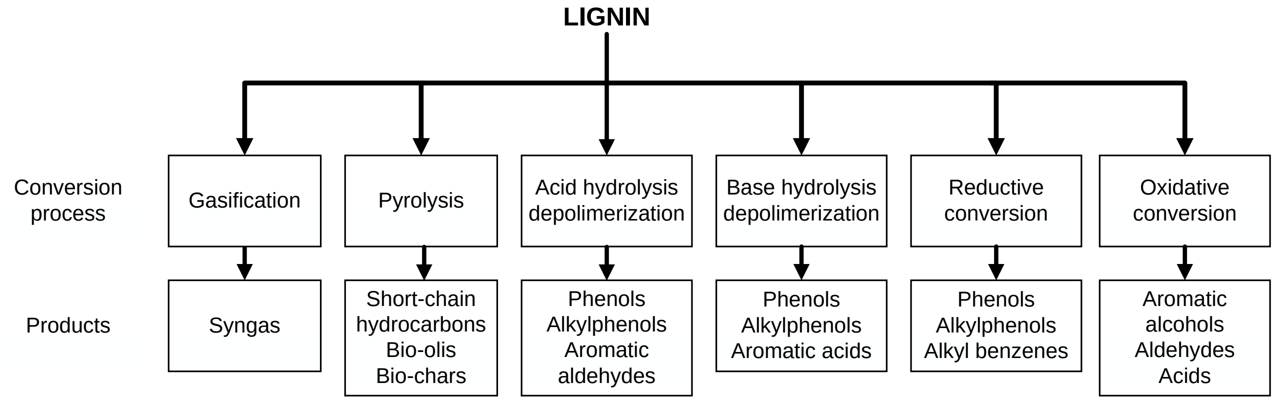

Figure 1. Lignin valorization processes and lignin-based intermediates/products.

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WS2 PO13

[OSSO]-Type Iron (III) complex for the ring opening polymerization of cyclic esters

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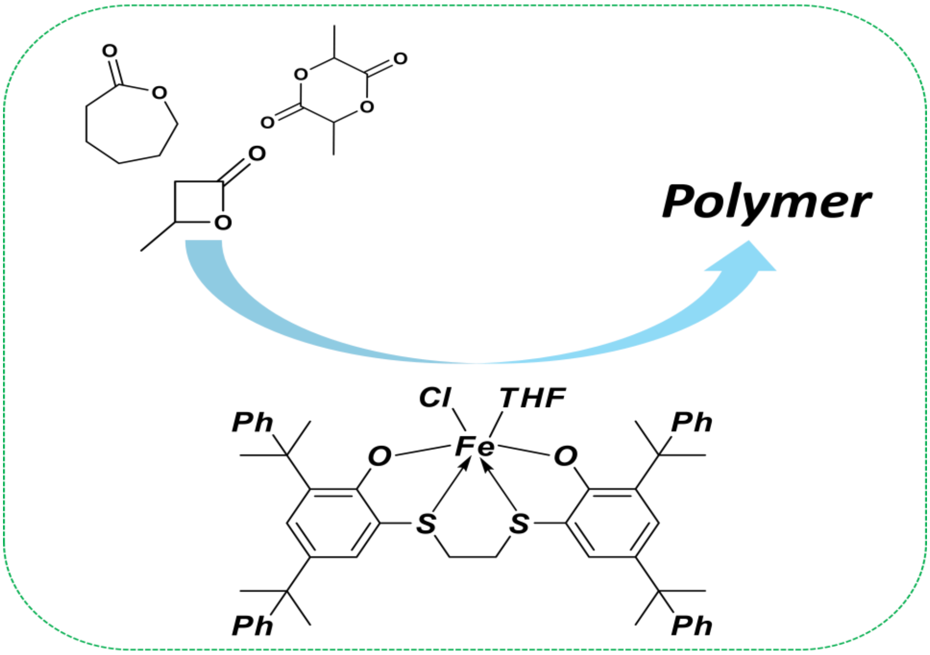
Nowadays, about 350 million of tons of plastics are produced annually all over the world and most of these plastics are of petroleum origin. The environmental and economic problems related to the petrochemical-derived polymers have driven the academic research toward the development of green and degradable alternatives to conventional plastics.(1) The biodegradable polymers, for example aliphatic polyesters, can be considered safe for the environment and an interesting alternative to conventional polymers. One of the most efficient methods to synthesize aliphatic polyesters, such as polylactic acid and poly-β-hydroxybutyrate, is the ring opening polymerization (ROP) of cyclic esters initiated by coordination compounds.(2) In literature many metal based complexes have been reported to promote this reaction but few of these are based on iron although this element is widely available, cost effective and non-toxic. This work explores the catalytic performances of an iron complex featuring a tetradentate (OSSO)-type bis(phenolato) ligand (3) in ring opening polymerization of *rac-lactide*, *β-butyrolactone* and *caprolactone*. The activities compares well with those reported for most active iron complexes.(4) Interestingly, the MALDI-TOF-MS investigations on the resulting polymeric structures revealed the highly selective formation of cyclic polymers.



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WS2 PO14

Biocatalysis for the synthesis and functionalization of renewable polymers and composite materials: taking inspiration from nature

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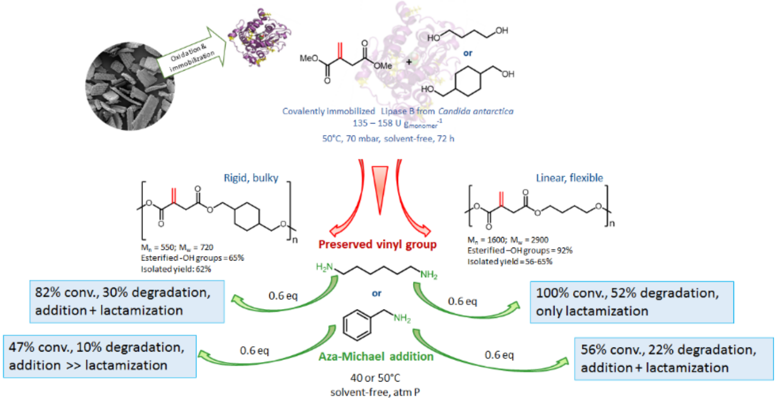
The feasibility of enzymatic polycondensation of dimethyl itaconate with either linear 1,4-butanediol or the rigid and bulky cyclohexanedimethanol sets the basis for the exploitation of the bio-based unsaturated itaconic acid monomer as a chemical platform for new functionalyzed polyesters with controlled architectures and reactivities. The structural and experimental factors that must be controlled in order to exploit the aza-Michael addition of primary amines (hexamethylendiamine and 2-phenylethylamine) for obtaining poly(itaconate)s with functionalized side chains or, rather, for degrading the polyesters. Our results indicate that the rigidity of the co-monomer 1,4-cyclohexanedimethanol decreases the incidence of lactamization and the consequent degradation of PCI when reacted with hexamethylenediamine. The crucial role of chain rigidity was also confirmed by the faster degradation of the linear poly(1,4-butylene itaconate) (PBI) in the presence of both primary amines. We have demonstrated the applicability of functionalized rice husk as carrier for the covalent immobilization of lipase B from *Candida Antarctica* (1). This new renewable and inexpensive carrier proved to be more efficient than the fossil-based commercial methacrylic resins in the solvent-free polycondensation catalyzed by CaLB (2). The mild conditions of the reactions (50°C, 70 mbar and solvent-free) preserved the labile vinyl group of itaconic acid, but also the degradation of the 1,4-cyclohexanedimethanol was avoided, thus obtaining poly(itaconate)s with Mw, ranging from 720 to 2859 g mol^{-1}.



The immobilization of enzymes on renewable carriers opens new perspectives for overcoming the environmental impact of fossil-based carriers while boosting the economic viability of processes nowadays hampered by the high cost of immobilized biocatalysts. Moreover, the possibility to insert discrete units of itaconic acid in polyesters via enzymatic polycondensation opens new routes for the development of structurally complex bio-based functionalized materials not achievable through conventional chemistry (3).

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WS2 PO15

Transfer hydrogenolysis of lignin and its derived aromatic ethers promoted by the bimetallic Pd/Co catalyst

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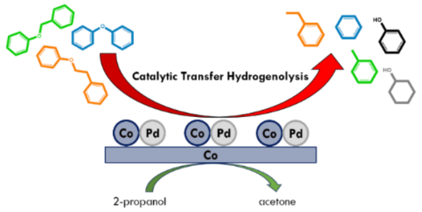
One of the major challenges in the catalytic valorization of lignin is the selective cleavage of the C–O bond (1, 2). Therefore, in order to develop selective catalytic processes for the production of aromatics from lignin, a complete understanding of the molecular aspects of the basic chemistry and reactivity of aromatic ethers is still crucial. A lot of research affords have been directed to the study of the catalytic hydrogenolysis of benzyl phenyl ether (BPE), phenethyl phenyl ether (PPE) and diphenyl ether (DPE) that are the simplest model molecules of α-O-4, β-O-4 and 4-O-5 lignin linkages.

Homogeneous and heterogeneous Ni-based catalysts have found, so far, a potential application in the hydrogenolysis of aromatic ethers (3, 4, 5). Hence, heterogeneous bimetallic catalysts have gained increasing attention for their enhanced activity and durability in different reactions (6).

CTH reactions has recently gained increased attention as an efficient alternative to the direct use of molecular hydrogen by improving the sustainability and economics of hydrogenation reactions (7, 8). In this context, to further explore the enhancement of the palladium activity promoted by other transition metals, the Pd/Co bimetallic catalyst was prepared by using the coprecipitation method and fully characterized by TEM, XRD, H_2-TPR, XPS and EXAFS.

By using Pd/Co as the catalyst and 2-propanol as the H- source, under batch conditions, an appreciable BPE (0.1 M) conversion was achieved after 90 minutes at 210 °C. The conversion of BPE increased by increasing the reaction temperature and it was fully converted at 240 °C. Transfer hydrogenolysis reactions over 2-phenethylphenylether (PPE) and diphenyl ether (DPE) were also investigated. Catalytic tests show that the cleavage of C-O bond of PPE and DPE is less efficient due to the higher bond dissociation energies (β-O-4 = 289 kJ/mol and 4-O-5 = 314 kJ/mol) involved.

Reactions carried out with the analogous Pd/Co catalysts prepared by using the impregnation method are by far less efficient. Therefore, the enhanced catalytic performance shown by Pd/Co catalyst can be related to the coprecipitation method that allows the formation of bimetallic PdCo ensembles that positively promote the C-O bond cleavage of aromatic ethers.



The last part is dedicated to the investigation of the transfer hydrogenolisysis reaction of lignin, obtained by organosolv processes, studying the relative conversion by means of 2D HSQC NMR, using the Pd/Co catalyst, in order to investigate the potential applicability in the direct valorization of lignocellulosic biomasses.

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WS2 PO16

Pretreatment of waste lignocellulosic biomasses aimed at their chemical valorization

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In the last few decades the concepts of sustainability and of circular economy grew in importance. The aim is to develop new processes able to minimize both the amount and the impact of the waste by reusing the greater part of products and byproducts (1). The present work has been carried out in the frame of the H2020 "FORCE – Cities Cooperating For Circular Economy" project which is rooted on such concepts and deals with innovative ways to reuse and exploit waste materials in four EU cities: Hamburg, Lisbon, Copenhagen and Genoa (2). The City of Genoa focuses on the subject matter of waste wood.

The goal was to develop a viable process able to transform different waste woods into higher value products through a double-step process (pretreatment and biotechnological treatment). The pretreatment step aims at reducing the recalcitrance of the lignocellulose fraction (3), while the treatment step ought to degrade the macromolecular structures composing it (cellulose, hemicellulose, lignin) into low molecular weight products (such as monosaccharides from cellulose and hemicellulose, various products including substituted phenols from lignin) (4).

Liquid Hot Water and *Steam Explosion* techniques were investigated as pretreatment step in different conditions (pressure, temperature, time, using both a commercial autoclave and a custom reactor. To handily compare different experiments, the Severity Factor (3,4) was used.

Morphological and structural changes were investigated by optical microscopy and field emission scanning electron microscopy (FESEM), whereas the surface area was determined by N_2 adsorption at 77 K. The biotechnological treatment was performed by Active Cells S.r.l. (Genoa) employing enzymes produced by *Trametes Versicolor*, *Penicillum spp*., *Trichoderma spp*. and *Aspergillus Niger*. Those fungi and molds were chosen according to their ability to produce cellulases, hemicellulases and lignin-modifying enzymes (3).

The aqueous solutions produced by the biotechnological treatment were characterized by means of Chemical Oxygen Demand (COD), total carbohydrates content through the phenol-sulfuric method (6) and total phenols content using the Folin-Ciocalteu method (7).

The pretreatment step has shown an increase in the surface area of the waste wood up to 15 times after moderate severity *Steam Explosion* pretreatment (log R_0 = 3,8-4,0) and the pretreated wood demonstrated itself a suitable substrate for the enzymatic hydrolysis. Currently, a sequential biotechnological treatment has shown to be the most promising, with a moderate conversion (typically 20%) but an interesting selectivity in fermentable sugars (>66%), higher than the previously attempted conversion routes.

This poster is also presented as BE PO14

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WS2 PO17

Enzymatic hydrolysis of lactose to exploit cheese whey as a source of chemical building blocks

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The use of agri-food waste (i.e. waste from agricultural and food industries) as raw material is a key point of bioeconomy (1). The dairy industry is one of the most relevant sectors of the Italian food industry and cheese represents its main product. Cheese whey (CW) is the main by-product of the cheese making (2). Due to its high content in lactose and proteins, CW is considered a pollutant waste and its direct release in the environment, without any pre-treatment, is forbidden. Lactose represents the main pollutant of CW and can be hydrolysed by chemical or enzymatic treatment (3). Here we proposed the use of a novel Antarctic β-galactosidase (β-Gal_M) for the enzymatic hydrolysis of CW lactose, to obtain glucose and galactose as building blocks for chemical transformations. Easily produced as a recombinant protein, β-Gal_M has proved to be a very stable enzyme, specific for the hydrolysis of β-galactoside bond. Furthermore, the activity in a broad range of temperature (from 5°C to 50°C) makes this enzyme suitable to investigate the exploitation of CW by lactose hydrolysis. According to circular economy principles, this type of process could be advantageous above all when realized in a context where CW, and the lactose it contains, represents an abundant resource, widely accessible but not yet fully exploited. This is the case of the CW produced in Lombardy and its by-products poor in proteins but rich in lactose.

WS2 PO18

FALstaff project: Fatty Acids from Lanolin. Waste wool wax as a source of fatty acids and valuable α-hydroxy fatty acids by integrated biocatalytic and sustainable physico-chemical methods

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The project integrates diversified expertises in organic chemistry, medicinal chemistry, biochemistry, microbiology, biocatalysis, materials, engineering and environmental sciences. The objective is the development of sustainable procedures to recover wool wax and lanolin from waste wool. In parallel, ecofriendly physical, chemical and/or biocatalytic methods are devised to exploit these products, recoverable from an abundant discarded biomass such as waste wool, as a source of fatty acids (FAs) and α-hydroxy fatty acids (α-HFAs), which are highly-value derivatives of FAs. Lanolin has a high content of both α-HFAs and FAs esters.

Therefore, the aim of the project is to conjugate the production of useful and valuable chemicals with the valorization of a biomass, otherwise to be disposed of. It is to be underlined that waste wool is unavoidably joined to sheep farming and its management costs. Waste wool scouring would become profitable if further valorization of lanolin could be associated to the uses of washed low-quality coarse wools.

Preliminary results of waste wool treatment and of FAs and α-HFAs obtainment are presented.

The project is financed by FONDAZIONE CARIPLO.

WS2 PO19

Towards Aerobic Catalytic Biomass Valorization: from simple models to lignin depolymerization

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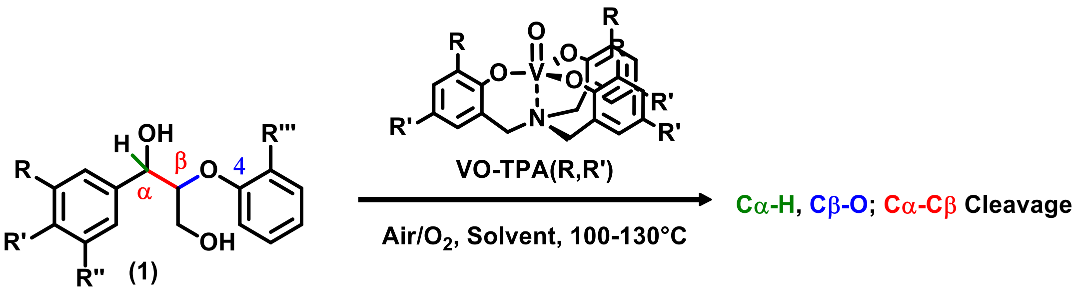
In recent years, valorization of non-food renewable carbon feedstocks has been gaining much more attention due to fossil fuels shortages (1). Among these alternative sources, lignin can be regarded as the most earth-abundant and cheapest natural source of aromatic compounds. All these factors contribute to make lignin valorization a very appealing process. However, despite its potential the production of fuels and chemicals, lignin remains the most poorly utilized lignocellulosic biomasses because of its complex polymeric structure, inert resistance to chemical reactivity and the lack of suitable conversion technologies. Therefore, selective lignin depolymerization to value-added aromatic products still remains a challenge (2). In particular, the development of robust catalysts that selectively target C-C bonds oxidative cleavage in lignin structure can be a key in overcoming the problem (3).
Recently, it emerged that V^V aminotriphenolate complexes (**VO-TPA(R,R')**) (4) are good candidates to achieve such ambitious goals in a very active and selective manner under rather mild reaction conditions (Figure 1).



In this communication, we therefore describe the catalytic activity of (**VO-TPA(R,R')**) in oxidative cleavage of lignin models, starting from simple diols and extending substrate complexity to models containing actual β-O-4 bonds **(1)**. In particular, we will report results about the optimization of reaction conditions and the selectivity with respect to the kind of cleavage that such systems can undergo (specifically Cα-Cβ vs Cβ-O vs Cα-H).

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WS2 PO20

Life cycle assessment of industrial syngas production: comparison between a new steam/dry reforming process and traditional routes

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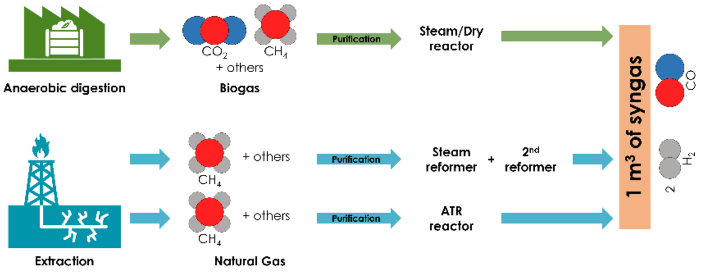

In the context of a circular economy, waste must be used as a source of raw material in order to reduce the risk associated with its management and contrast the exploitation of non-renewable resources. According to this approach, a new process of biogas upgrading has been studied, with the aim of replacing the current technology that involves the recovery of natural gas. The scope of this work is therefore to analyse and quantify, from a life cycle perspective, the environmental performance of a new route for the production of syngas from biogas, derived from the anaerobic digestion of organic waste. In order to assess its performance in reducing the environmental impact of the syngas production, this process has been compared with two traditional technologies, as illustrated in Figure 1. The set of reactions that characterize this type of transformations is essentially the same: steam reforming, dry reforming, water gas shift and catalytic partial oxidation. Depending on the type of input, the reagents and the reaction conditions, the balances will move towards the most favoured product. The three processes shown above use these reactions to obtain a final output in which the H_2/CO ratio is equal to 2 (characteristic of the syngas which could be used for subsequent processes, as methanol or Fischer-Tropsch synthesis). A brief description of the routes is given:

- <u>Steam/Dry reforming</u>: the innovative pathway that involves the use of biogas. The process combines the reaction of steam reforming and dry reforming in a single reactor, and is promising for the production of syngas;
- <u>Two-step reforming</u>: in this configuration, the steam reforming reactor is followed by a second "oxygen-fired adiabatic reforming reactor" (similar to an ATR reactor) which, by regulating the input of O_2 to the secondary reforming, adjusts the H_2/CO ratio of the output (1);
- <u>ATR</u>: the starting reagent is natural gas, which is sent to a reactor with two regions: a turbulent combustion zone where the partial oxidation of CH_4 occurs and a catalytic zone where heterogeneous catalytic reactions (water gas shift and steam reaction) take place. By adjusting the steam/oxygen ratio inlet, it is possible to adjust the composition of the output syngas (2).

Two-step reforming and ATR are processes already set at industrial level and applicable for the production of syngas from natural gas, while the Steam/Dry reforming of biogas is still in the development phase. Therefore, to simulate the process of this last scenario Aspen Hysys was used, in order to obtain system boundaries consistent with others and make them comparable.

The LCA (Life Cycle Assessment) methodology was used as a scientific tool of analysis and environmental assessment to estimate the impact of the production of 1 m^3 of syngas through the three different routes. The environmental impact of the emissions and the consumption of resources were evaluated respectively with the ReCiPe and CED methods of the SimaPro software (see 8.5), using Ecoinvent (see 3.1) as the database for the calculation.

Reference: 1. L. Chen, P. Gangadharan, H. H. Lou, *Asia-Pac J. Chem. Eng.*, **2018**, 13:e2168. 2. W. Maqbool, E. S. Lee, *Chem. Eng. Technol.*, **2014**, 37, No. 6, 995–1001.

WS2 PO21

Biochar: a new carbon filler for composite able to improve electrical and mechanical properties

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The use of biomasses in the field of composite materials are became a new trend. Several advantages are correlated to this issue. Recycling and improving of composite properties are some examples. Carbonized biomasses (Biochar) represent an ideal carbon based filler to use in composite when an alternative to oil based carbon material is required. In this work we report recent developments on the study of biochar as filler in polymer composite materials to improve mechanical (1) and electrical (2) properties. A glance on the possibility represented by this bio based materials derived from waste biomasses used in the production of composites will be also reported.

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WS3 - SMART PEPTIDE CHEMISTRY FOR NEXT GENERATION INDUSTRY IN A SUSTAINABLE SOCIETY

In the last 5 years peptide science went through a real renaissance, raising a constantly increasing interest from research scientists and industry. Pharmaceutical, diagnostic, cosmetic and well-being industries are the main stakeholders for the development of new peptide-based materials, and sustainable synthetic methods for their large-scale preparation.

The launch on the market of these products prompted a large R&D effort. Aim of the workshop is to put in communication peptide science researchers and stakeholders from industry and society, to explore the possibility of application of peptide materials in many diverse fields with potential societal impact, from antimicrobial resistance to culture heritage to nutraceuticals.

WS3 - Scientific Committee and Conveners

CONVENERS

- Annamaria Papini (University of Florence)
- Giancarlo Morelli (University of Naples)
- Luis Moroder (Max Planck Institut for Biochemistry, Germany)
- Timo Nuijens (EnzyPep B.V.- Fresenius Kabi)

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- Anna Maria D'Ursi (University of Salerno)
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- Anna Maria Papini (University of Florence)
- Paolo Rovero (University of Florence)
- Mariano Venanzi (University of Rome Tor Vergata)

WS3 - Keynote and Invited Lectures

- **WS3 KN01** – Antonio Ricci, Fresenius Kabi, “*Therapeutic peptide API manufacturing production: an industry perspective*”.
- **WS3 KN02** – Michele Saviano, CNR, Bari, “*Molecular Targeting for Precision Medicine*”.
- **WS3 IL01** – Michael Chorev, Harvard Medical School, “*Disease-relevant post-translationally non-enzymatically modified biomarker – a challenge and its solution*”.
- **WS3 IL02** – Timo Nuijens, Enzypep, Netherlands, “*Efficient chemo-enzymatic synthesis (CEPS) of incretin peptides*”.

WS3 KN01

Therapeutic peptide API manufacturing production: an industry perspective

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Therapeutic peptides market is exponentially increasing in the recent years. This trend is confirmed by the number of peptide product approved for the worldwide market (60), and the consistent number of 155 peptides currently in clinical trials. On the other side, the complexity of the peptide APIs present in the late stage of the marketing approval process is growing in a similar way, witnessed by the increased average number of aminoacid and non-natural residues (both side chain or non-natural aminoacid) in the peptides enrolled as candidates for clinical trials(1). This aspect triggered the attention of the Academia and the Pharmaceutical Industry sectors to joint efforts towards the development of innovative synthetical routes for the manufacturing of these products, comprising both the Upstream (synthesis of the crude peptide API) and Downstream (purification and isolation the pure peptide API). The manufacturing routes must fulfil the requirements of the market, such as high product quality at an effective cost price, but should also be innovative respect to the known prior art, as to guarantee the freedom to operate and avoid any patent infringment. Furthermore, increased attention is gained to the development of environmental friendly and sustainable approaches (2), which look at a reduction of the amount of solvents and loss of yield, keeping, even if not improving, the quality of the target peptide.
Herein, all these aspects were discussed through case studies occurred in our laboratory (3) during the development of the manufacturing processes for our peptide API targets.

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WS3 KN02

Molecular Targeting for Precision Medicine

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A great challenge in cancer therapy is the selective delivery of anticancer agents or radiotherapeutics to tumour cells reducing the side effects on normal cells. To further improve delivery efficiency and cancer specificity, great efforts have been dedicated to the development of effective systems that can actively target tumours through the molecular recognition of unique cancer-specific "markers" that are overexpressed in the cancerous tissues.

The use of peptides as targeting tools has been validated in a number of applications. Examples are radio-labelled peptides used to deliver radio-therapeutic doses to cancer tissues. In this case a cytotoxic entity, such as a radionuclide or a chemotherapeutic drug is driven by the peptide to the transformed cells with higher efficacy than to normal cells. Typically such conjugates, at lower doses, have useful applications for diagnostic applications whereby they are used to visualize even small lesions due to the overexpression of tumour genes.

Often, such conjugates can have poor delivery properties, because of intrinsic high hydrophilicity. However, over the past several years, an explosive development of nanovectors (i.e micelles, liposomes) usable in drug delivery and molecular imaging applications have been reported. Nanoscopic therapeutic systems that incorporate therapeutic agents with molecular targeting capabilities are emerging to improve the therapeutic outcome of drug therapy, but even to improve diagnostic outcomes.

In this lecture, we will present our most recent results on a project that aim at the rational design of targeting peptidomimetic ligands to specific tumour receptors (1, 2, 3, 4, 5, 6, 7, 8).

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WS3 IL01

Disease-relevant post-translationally non-enzymatically modified biomarker - a challenge and its solution

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CD59 is a 70kD GPI-linked membrane-anchored complement regulatory protein that is ubiquitously expressed extracellularly on mammalian cell surfaces and functions as a specific inhibitor of membrane attack complex (MAC) formation. As such, it is the last of several soluble and membrane-bound complement regulatory proteins in the complement system to protect "self" cells from the damaging consequences of unrestricted complement activation. Strong clinical and experimental evidence support the association between the complement system and the pathological manifestations of diabetic complications (1). The presence of K^{41}/H^{44}, a glycation motif at proximity to W^{40}, the active site of CD59, predestines CD59 to glycation inactivation (2, 3). Frequent and protracted hyperglycemia as presented in prediabetes, diabetes and gestational diabetes results in expansion of glycation inactivation of CD59 leading to increased generation of MAC causing lysis of RBCs, activation of intracellular signaling pathways and release of cytokines and growth factors that promote inflammation, proliferation and thrombosis as typically observed in the target organs of diabetes complication (2). Our laboratory has developed the molecular tools and methodology that enable the construction of an ELISA assay that measures quantitatively the levels of glycated CD59 (GCD59) in plasma (4, 5). These tools included the antigens, the corresponding mono-clonal antibodies and last but not least the GCD59 surrogate which, in the absence of the unattainable endogenous GCD59, serves as an effective calibrator. Measurement of the GCD59 biomarker allows screening cohort of pregnant individuals to differentiate with high specificity and sensitivity between those at low- and high-risk of presenting gestational diabetes (6). GCD59, our novel biomarker is positioned to fulfill an urgent unmet need for a reliable and disease-relevant biomarker that is accurate, simple and convenient to be used in screening for gestational diabetes.

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WS3 IL02

Efficient chemo-enzymatic synthesis (CEPS) of incretin peptides

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The increasing number of marketed and (pre-)clinical incretin mimic peptide therapeutics, used for the treatment of diabetes type II and obesity, mandates the development of efficient and cost-effective routes for their manufacture. Currently, both lab scale synthesis and efficient large scale manufacture of (acylated) peptides over 30 amino acids is still challenging. Overall yield is often low, mainly due to the demand for high purity of the final product. Due to their inherent favourable properties, the use of enzymes for the efficient synthesis of (acylated) peptides represents a promising strategy and provides an elegant link between chemistry and biology.(1, 2) Over the past years, we have developed several subtilisin variants, termed peptiligases, that are capable of forming a peptide bond between a *C*-terminal (glycolate) ester fragment and the *N*-terminus of an acyl acceptor fragment with high efficiency. (3) An enzymatic fragment based strategy for the synthesis of (long) peptides usually leads to less impurities and a higher overall yield as compared to full SPS.

Herein, we report the efficient chemo-enzymatic peptide synthesis (CEPS) of block-buster incretin peptides, such as Exenatide. Specific items discussed will be the optimal ligation strategy, SPPS of the fragments, enzymatic ligation, overall efficiency of the CEPS process and scale-up. In general, the overall yield for the production of incretin peptides using CEPS is more than doubled as compared to full SPPS.

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WS3 - Oral Communication

- **WS3 OR01** – Maria Vittoria Barone (University of Naples) *“Gliadin Peptide P31-43 as Trigger of the Proliferative and Stress/Innate Immune Response of the Celiac Small Intestinal Mucosa”*
- **WS3 OR02** – Fosca Errante (University of Florence) *“Anti-ageing peptides derived from serpin A1 for cosmeceutical uses”*
- **WS3 OR03** – Fernando Formaggio (University of Padua) *“Chemical modifications to improve peptide enzymatic stability”*
- **WS3 OR04** – Emanuela Gatto (University of Rome Tor Vergata) *“Novel Peptide Bioinspired and biodegradable approach for solar energy conversion”*
- **WS3 OR05** – Giancarlo Morelli (CIRPEB, University of Naples ‘Federico II’) *“Easy formulation of liposomal Doxorubicin modified with a Bombesin peptide analogue for selective targeting of GRP receptors over-expressed by cancer cells”*
- **WS3 OR06** – Maria Luisa Nolli (NCNbio) *“Biodrugs and advanced therapy medicinal products: a revolution in medicine”*
- **WS3 OR07** – Giacomo Pepe (University of Salerno) *“The health promoting potential of buffalo ricotta cheese-derived peptides”*
- **WS3 OR08** – Paolo Rovero (University of Florence) *“The Industry-University Joint Laboratory for the Synthesis of Peptides of Pharmaceutical Interest (PeptFarm): a new efficient tool for technology transfer at the University of Florence”*

WS3 OR01

Gliadin Peptide P31-43 as Trigger of the Proliferative and Stress/Innate Immune Response of the Celiac Small Intestinal Mucosa

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Ingested food can cause tissue inflammation through different mechanisms. In the intestine, and particularly in the enterocyte, nutrients are modulators of various cellular functions and may be involved in tissue immune response and inflammation. An example of an intestinal inflammatory and remodeling response of the intestine to food is the small intestinal celiac lesion induced by gluten, an alimentary protein present in wheat and other cereals. Celiac disease (CD) is characterized by inflammatory and structural changes resulting in remodeling of the small intestinal mucosa. Gliadin, the major protein component of wheat and other cereals, is a peculiar protein very rich in glutamine and proline. Several gliadin peptides are recognized by T-cells (TC) of the celiac intestine, and can induce the adaptive immune response, but most of them are digested by gastric, pancreatic and intestinal proteases. Only two main peptides remain undigested: the 33-mer (P55–87) and the 25-mer (P31–55). Consequently, these two peptides are the main peptides that are active in vivo in the celiac intestine after gluten ingestion (1).The inflammation of the intestinal mucosa is due not only to the adaptive but also to the innate immune responses to wheat gliadin. The A-gliadin 33-mer that is deamidated by tissue transglutaminase (tTG), binds to human leukocyte antigen (HLA) DQ2 and/or DQ8 and induces an adaptive Th1 pro-inflammatory response. The P31–43 peptide, which is contained in the 25-mer, is not recognized by TC (2) in the celiac intestine and is able to damage the celiac intestinal mucosa in vitro and in vivo. Moreover, the P31–43 gliadin peptide is able to initiate both a stress and an innate immune response with interleukin-15 (IL-15) as a major mediator (3). Although the structural changes of the celiac mucosa are considered a consequence of sustained mucosal inflammation due to the Th1-TC response, recent data have shown that gliadin peptides, in particular P31–43, induce proliferation and other effects in celiac enterocytes. These processes have profound effects in inducing the crypt hyperplasia, which is characteristic of the remodeling of the celiac mucosa. Moreover, gliadin peptide P31-43 induce alterations of structure (cell shape, actin modifications, increased permeability and vesicular trafficking alterations), signaling and proliferation and stress/innate immunity activation in several cell lines. Taken together, these data suggest that gliadin peptides (i.e., P31–43) can have several different non-T cell mediated effects, both in cell lines and cells and in biopsies from CD patients, that can be grouped into three sets: cell structural changes, including signaling/proliferative effects and stress/innate immunity activation. How these mechanisms of disease are related to the genetics of CD is still unclear.

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WS3 OR02

Anti-ageing peptides derived from serpin A1 for cosmeceutical uses

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The term "cosmeceutical" identifies a hybrid category of topical products lying between drugs and cosmetics. These products are not tested and approved as drugs, although they may contain different active ingredients, including peptides (1). However, it is not very common to find scientific literature supporting the claimed benefit.

In this scenario, Espikem Srl, traditionally active in the field of bioactive peptides, started, with the support of the Tuscany Region (POR FESR), an R&D project aimed at developing peptide active ingredients of proven activity for cosmeceutical use.

We focused our attention on serpin A1, which is part of the serpins family, proteins endowed with anti-protease activity. Following to a preliminary report on the activity of the C-terminal portion of this protein (2), we showed that the decapeptide SA1-III is able to modulate collagen type I turnover in cultured human fibroblasts (3).

With the purpose of investigating the mechanism of action of SA1-III, we synthesized four partially overlapping tetrapeptide fragments of this peptide, using the solid-phase strategy, followed by chromatographic purification and analytical characterization by HPLC-MS. All the peptides were used for *in vitro* studies on cell cultures derived from neonatal human dermal fibroblasts (NHDFs), in order to determine the concentrations of collagen type I produced in the presence of each tetrapeptide, in comparison with the basal concentration of collagen, measured in untreated fibroblasts.

We performed Western blot test on culture medium derived from fibroblasts treated with the peptides, as well as in cell lysates, analysing specific protein bands, i.e. those related to the procollagen forms, which is the precursor of collagen type I, and collagen degraded by proteases released by fibroblasts in culture media. This analysis showed that the mechanism of action leading to increased concentration of collagen type I in cell treated with both SA1-III and its derivatives is an anti-protease action rather than a stimulation of de novo collagen synthesis (4). In particular, we assessed a significant ($p < 0.05$) activity of peptides SA1-III and one of the tetrapeptides.

We are now planning skin permeability assays with the Franz cell apparatus and possibly formulation of liposomes or other vehicles to enhance skin permeation. In the meantime, we contributed to the launch on the market of an anti-age cream (Kp1, Apotech Srl) based on an active ingredient, whose proven effect is to modulate collagen turnover, by inhibiting the degradation component.

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WS3 OR03

Chemical modifications to improve peptide enzymatic stability

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Over the next five years the peptide therapeutics market will register a 5.5% growth of revenues, reaching US$ 39300 million by 2024, from US$ 28500 million in 2019 (1). The main request for the large-scale production of peptides comes from pharmaceutical companies, although peptides are likely to find relevant applications in agriculture, food and materials. The interest in peptides as pharmaceuticals is primarily due to their biodegradability and low toxicity. In addition, the easiness by which they can be modified ensures a very high target selectivity (2).

Relatively short peptides (up to 30 residues) can be obtained via chemical synthesis. This manufacturing technology allows for the synthesis of molecules with uniform chemical nature, thus accelerating both market launch and preclinical testing.

However, peptides suffer from some disadvantages such as low physical stability, oxidation of sensitive residues, hydrolysis of peptide bonds, aggregate formation. Also, in some cases peptides do not reach their molecular target because unable of penetrating the biological membranes (2).

Nevertheless, peptide drugs have gained relevance in the market as some disadvantages have been overcome in the last years. In this connection, the present communication will highlight a selection of chemical modifications used to impart the peptides with greater resistance to the enzymatic hydrolysis, without significant loss of biological activity.

In particular:

(i) N-terminal acylation and C-terminal amidation, that limit the action of exopeptidases;
(ii) replacement of selected L-amino acids by their enantiomeric D-amino acids;
(iii) N-to-C-terminus cyclization;
(iv) side-chain to side-chain cyclizations (stapled peptides);
(v) N- or O-glycosylation;
(vi) conjugation to blood plasma proteins (e.g. albumin);
(vii) conjugation to fatty acids.

An alternative approach, based on the introduction of backbone-modified amino acids, natural or unnatural, will be also presented by illustrating relevant examples of peptides already in the market.

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WS3 OR04

Novel Peptide Bioinspired and biodegradable approach for solar energy conversion

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The organization of molecules on surface is a key technological step toward further development of photoelectric conversion devices.

Previous work on dye sensitized solar cells (DSSC) showed that the possibility to covalently link organic dyes on the metal oxide surface, to control the formation of molecular aggregates and the directionality of the Electron Transfer (ET) process from the excited state were the key to improve the photoconversion efficiency. In nature plants use lipoproteins as template to organize chlorophyll dyes in an optimal arrangement, in order to avoid strong intermolecular interactions and to confer directionality to the ET process. One of the strategies employed for following the nature teaching is the immobilization of photosynthetic proteins on gold and TiO_2 surfaces. Photosystems I and II, and photosynthetic proteins have been successfully used as bioinspired devices for photoelectric conversion, but their low stability under thermal conditions, once extracted from their source, severely limits their use. With an alternative approach, helical peptide self-assembled monolayers have been proposed as promising materials for very efficient photocurrent generation.(1, 2) By using peptides all the advantages of protein materials are maintained (templating properties, capability of the electrons to travel over long distances, charge recombination hindering), while adding the capability of the system to self organize on the surface in an ordered manner, creating an oriented two dimensional array, thus increasing the molecular density on the surface and assuring ET directionality.

In this contribution, we will report on the design, characterization and properties of selected bio-inspired materials and highlight their potential for applications in optoelectronic devices able to generate current under light illumination (3, 4).

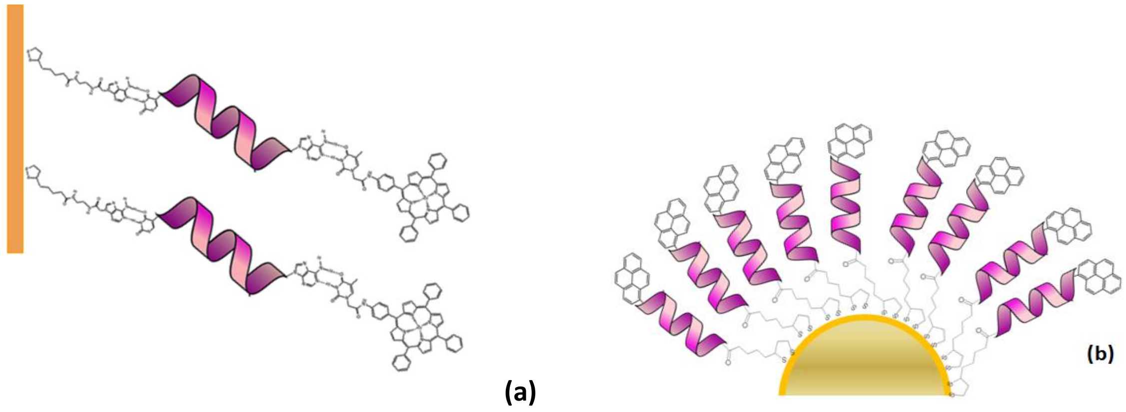

Figure 1. (a) DNA/peptide inspired film on gold surface functionalized with a light-absorbing group (a zinc-tetraphenylporphyrin chromophore) used as light harvester. (b) Titanium/gold nanoparticles functionalized by optically-active peptides constituting the harvesting unit of a dye-sensitized solar cell.

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WS3 OR05

Easy formulation of liposomal Doxorubicin modified with a Bombesin peptide analogue for selective targeting of GRP receptors over-expressed by cancer cells

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The presentation concerns the obtainment of liposomal doxorubicin (Dox) in which liposomes are externally modified with a targeting peptide able to drive the formulated drug in a selective way on membrane receptors overexpressed in tumours. We report on the development of a kit composed by three different vials: (A) a first vial containing a sterile, translucent, red dispersion of the liposomal doxorubicin drug, (B) a second vial filled with a lyophilized powder of a modified phospholipid with a reactive function (DSPE-Peg-maleimide), and (C) a third vial containing a 1-9 Bombesin peptide analogue (Cys-BN-AA1) chemically modified to react, in stoichiometric ratio, with the DSPE-Peg-maleimide after its post-insertion in liposomes.

The peptide, a stable analogue of the wild-type 1-9 Bombesin peptide, has been chosen (1) on the basis of in-vitro and in-vivo results by screening a peptide library for its ability to remain stable in serum and presenting high specifity, with nanomolar affinity, toward Gastrin Release Peptide Receptors (GRPRs also indicated as BB2), over-expressed in some cancer cells (2). Moreover, this peptide acts as a Bombesin antagonist, thus it does not interfere with biological pathways promoted by the Bombesin peptide. By using the kit product it is very easy to prepare, also at industrial level, a final product containing pegylated liposomal doxorubicin modified with the Bombesin analogue, Doxil-BN-AA1.

Results on animal studies clearly indicate that in mice treated with the kit product tumor growth is reduced, with an improved efficacy respect to mice treated with non-modified Pegylated liposomal Dox or with saline solution. (3).

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WS3 OR06

Biodrugs and advanced therapy medicinal products: a revolution in medicine

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Biotech drugs are the protagonists of the new frontiers of medicine. We are witnessing a real revolution in the health sector: innovative monoclonal antibodies and cell-based products as cell and gene therapies are able to cure diseases otherwise not curable with the traditional drugs. We are witnessing a switch from blockbuster drugs to niche busters and autologous therapies through the research and development of new biomarkers, which allow to select the best responder patients towards a personalized and precision medicine concept. Deriving from biological sources, these new drugs are completely different from the synthetic small molecules: they require a more complex and tailored process of development and production with sophisticated and innovative QC tests to assure the quality of the product to the patients.

WS3 OR07

The health promoting potential of buffalo ricotta cheese-derived peptides

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Buffalo milk contributes to 13% of the world milk production and is abundantly produced in Southern Italy regions. Buffalo milk is appreciated for its nutritive properties and is highly suitable for the manufacturing of wide range of dairy products. Several studies showed many bioactive peptides in different dairy species such as bovine, ovine and caprine milk, but few studies have been conducted on the buffalo dairy products (1). The present work is focused on the identification of bioactive peptides released after *in vitro* simulated gastrointestinal digestion of protein fraction isolated from buffalo-milk dairy products by ultra- and nanofiltration pilot plant.

The gastrointestinal digests of protein fractions were monitored by RP-UHPLC-DAD, while, the peptide identification was carried out by UHPLC-Orbitrap-based tandem mass spectrometry. 165 peptides were identified in Yoghurt, 152 in Scamorza, 146 in Mozzarella, 136 in Grana and Ricotta and 120 in Ice Cream samples (1). The peptides belong to both buffalo caseins (αs1-, β-, k-CN) and whey proteins (α-LA, β-LG).

Six G.I. digests of dairy products were tested in a model of oxidative stress using IEC-6 cells. Among them, buffalo ricotta cheese was the most active. UHPLC-PDA-MS/MS analysis revealed the presence of two abundant β-lactoglobulin peptides (BRP: YVEELKPTPEGDL, f:60-72 and BRP2: SFNPTQL, f:168-174). To confirm the hypothesized chemical structures and study their specific biological activity, the peptides were synthesized by conventional solid-phase peptide synthesis methods. The antioxidant potential of the identified peptides was then evaluated in a model of hydrogen peroxide induced oxidative stress in IEC-6 cell line. The peptides reduce ROS release and increase nuclear factor (erythroid-derived 2)-like 2 activation and the expression of antioxidant cytoprotective factors such as heme oxygenase 1, NAD(P)H: quinone oxidoreductase 1 and superoxide dismutase (2). The bioavailability of β-lactoglobulin peptides was evaluated in intestinal transport studies through Caco-2 cell monolayer. Only BRP2 showed equal bi-directional transport and linear permeability, suggesting that it was mainly absorbed through passive diffusion. In addition to its local effects, administration of BPR2 on mice mesenteric arteries counteracts the Angiotensin II-induced vasoconstriction by Nrf2 nuclear translocation, reduction of active form of Ras-related C3 botulinum toxin substrate 1 (Rac1) and NADPH oxidase activity. The analysis at molecular level of treated vessels showed an induction of Nrf2 translocation to nucleus associated with increased expression of MnSOD and Rac1 deactivation.

The data indicate how protein fraction of buffalo ricotta cheese could be an important source of antioxidant compounds, as well as YVEELKPTPEGDL and SFNPTQL peptides could be considered as an "ingredient" for nutraceuticals formulations and functional and personalized foods, in order to prevent the onset of some gastrointestinal pathologies and cardiovascular diseases.

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WS3 OR08

The Industry-University Joint Laboratory for the Synthesis of Peptides of Pharmaceutical Interest (PeptFarm): a new efficient tool for technology transfer at the University of Florence

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Over the past decade, peptide drug discovery has experienced a revival of interest, as the pharmaceutical industry has come to appreciate the role that peptide therapeutics can play in addressing unmet medical needs and how this class of compounds can be an excellent complement or even a preferable alternative to both small molecule and biological therapeutics (1).

However, large-scale synthesis of peptide Active Pharmaceutical Ingredients (APIs) under GMP conditions is still a challenge (2), in spite of the R&D effort done by a few specialized companies since the approval of the antiretroviral peptide Enfuvirtide (Fuzeon, Roche) for the treatment of HIV infection in 2003. In fact, a key enabling technology routinely used in the field of peptide science, i.e. the synthetic method based on Merrifield solid-phase strategy (3), is inherently not easily scalable. Moreover, since peptide APIs are regarded at the regulatory level as laying at the border between conventional chemical molecules and biological entities, we observe a lack of guidelines for clear and harmonized regulation of peptide drugs, resulting in a regulatory vacuum, which presents a further challenge to peptide manufacturers (4).

In this scenario, API producers interested in entering into the peptide arena need to acquire specialized R&D capabilities, both in term of staff and equipment, while the academic research groups active in the field of bioactive peptides may show limited interest for an R&D effort directed toward process chemistry.

An effective answer to this dilemma has been provided in our University with the implementation in 2017 of the "Industry-University Joint Laboratory for the Synthesis of Peptides of Pharmaceutical Interest" (PeptFarm), establishing a strong collaboration between our research laboratory, active for many years in the field of bioactive peptides, and a leading Italian API producer. In fact, the PeptFarm Joint Laboratory, founded with a formal agreement between the University of Florence and the partner company, is a fully equipped physical space, located within the University facilities, in which permanent staff from both the University and the partner company work to specific R&D projects of industrial interest, under the supervision of a joint steering committee.

In particular, the two main missions of PeptFarm are: (i) development of robust and scalable synthetic methods for the preparation and qualification of specific peptide APIs, with particular attention to the use of microwave-assisted large-scale solid-phase peptide synthesis methods, to be transferred to the GMP facility of the partner company, and (ii) staff training.

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WS3 - Poster Communications

- **WS3 PO01 -** Barbara Biondi (CNR, University of Padua) "*SPPS alternative strategies for the production of Degarelix*"
- **WS3 PO02 -** Annunziata D'Ercole (University of Florence) "*Development of new approaches to alternative cyclization strategies from lab scale to pilot scale production of peptides. Academic research of constrained lead peptides for long-term industrial development.*"
- **WS3 PO03 -** Fernando Formaggio (University of Padua) "*Covalent grafting of lipopeptides on cotton fibers*"
- **WS3 PO04 -** Emanuela Gatto (University of Rome Tor Vergata) "*2D and 3D peptide nanostructures for health, sensing and solar energy conversion*"
- **WS3 PO05 -** Manuela Grimaldi (University of Salerno) "*Characterization of Lanreotide Autogel using combination of imaging and magic angle spinning NMR spectroscopy with atomic force microscopy*"
- **WS3 PO06 -** A. Mazzoleni (University of Florence) "*N-glucosylated peptide conjugates for an antigen-specific immunotherapy of multiple sclerosis*"
- **WS3 PO07 -** Olivier Monasson (University of Paris.Seine) "*Peptlab@UCP: a prototype platform for cGMP large scale peptide synthesis to favour phase I and II clinical studies*"
- **WS3 PO08 -** Giacomo Pepe (University of Salerno) "*Novel decameric peptide of Spirulina platensis with potent in vivo antihypertensive activity*"

WS3 PO01

SPPS alternative strategies for the production of Degarelix

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Degarelix is an antagonist of the gonadotropin-releasing hormone used as first-line treatment drug in prostate cancer[1]. The synthesis of the 10-mer peptide is complicated by the presence in its sequence of several non-natural α-amino acids, which are susceptible to side reactions and rearrangements.
One of the most problematic residue is the dihydroorotic (Hor) moiety in Aph(Hor) which, in presence of bases, rearranges with subsequent hydantoin formation.
Here, we describe innovative synthetic strategies to overcome this problem. In particular, we tested a set of different organic bases which afford rapid Fmoc deprotection, and prevent the rearrangement of Hor moiety. In our second approach, we carried out the complete synthesis of Degarelix using a *p*-NO_2-Phe residue in place of Aph(Hor), completely avoiding the contact of Hor with the bases, and introducing the Hor moiety at the last step of the synthesis.
Both the strategies allowed us to obtain Degarelix in good yields and high purity.

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WS3 PO02

Development of new approaches to alternative cyclization strategies from lab scale to pilot scale production of peptides. Academic research of constrained *lead peptides* for long-term industrial development.

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Therapeutic needs are moving scientists toward new well tolerated, safe, and efficient Active Pharmaceutical Ingredients (APIs). Several peptides have been already demonstrated having many of these properties compared to small molecules. Therefore they are already on the market in a wide range of applications. The expected annual growth for the sale of peptide drugs is about 9-10%, which would exceed 70 billion USD in 2019 (1). Since, patents of many peptide drugs are expiring and a large number of new peptide drugs are going to enter the market, CMO sector is working at sustained rates to meet the current need for large quantities/year of peptide APIs, with the aim to reduce production cost. Our collaboration between FIS and PeptLab performed in the joint laboratory PeptFarm is aimed to industrial optimization of robust and competitive synthetic and purification procedures, compatible with kilo-scale production. On the other hand, industrial production can become an alternative and sustainable source of sponsoring research projects aimed to the development of new peptide drug. However, peptide APIs manufacturing requires full compliance with GMP regulations and FDA guidelines. In this context, many are the challenges that pharmaceutical companies have to face. It is estimated that nowadays about 60 new peptides available on the market are produced by Fmoc/tBu solid-phase (SPPS) strategies (2, 3), which do not require intermediate isolation, simplifying the process and saving time. The physico-chemical characteristics of the resin used for SPPS, as well as the substitution grade and distribution of the anchoring sites, the amino acid sequence and possible solubility problems and/or aggregation properties of the growing peptide chain can dramatically affect both coupling and deprotection reactions. Constrained structures such as cyclopeptides (4) can have additional synthetic problems to solve. Different cyclization strategies have been proposed but not all of them are suitable for industrial production (5, 6). This PhD project aims to identify alternative microwave-assisted solid-phase cyclization processes to overcome the limits of kilo-scale production ensuring high yield, reasonable crude purity at limited costs for final extensive purification.

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WS3 PO03

Covalent grafting of lipopeptides on cotton fibers

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Bacterial proliferation in health environments is currently a major concern as it may lead to the development of specific allergies and pathologies. In particular, infections during chemotherapy can be highly dangerous. In this contribution we present the preparation and characterization of a cotton-based textile, characterized by the covalent attachment of lipopeptides. We aim at assessing the possibility to produce safe and biocompatible materials endowed with a durable antimicrobial action (1, 2, 3).

As possible antimicrobial agents we selected a few lipo-tetrapeptides, whereas cotton was chosen in view of its widespread use in health care environments.

The membrane disruption action of peptides often requires the formation of clusters. Therefore, we also synthesized and linked to the cotton a few dendrimers (4) of our lipo-tetrapeptides.

They were immobilized onto the cotton fabrics through a covalent link, according to protocols previously established (1, 2). The covalent attachment should impart resistance to repeated washings and use.

In previous contributions (1, 3) we exploited FT-IR and the electron paramagnetic resonance (EPR) to characterize the new textiles. In this case we introduced also the X-ray photoelectron spectroscopy (XPS) to analyze our cotton-peptide conjugates.

We also performed a preliminary investigation of the antimicrobial activity against Staphylococcus aureus (Gram positive) and Escherichia coli (Gram negative) bacteria. Promising results were obtained against the Gram positive strain, responsible for most hospital-acquired infections.

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WS3 PO04

2D and 3D peptide nanostructures for health, sensing and solar energy conversion

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Nature has evolutionary developed highly efficient processes through spontaneous self-assembly of functional nanostructures. Bio-inspired materials have the great advantage to be biodegradable, biocompatible and produced by sustainable chemistry and mild experimental conditions. The growth of supramolecular assemblies can be thermodynamically or kinetically controlled, and the aggregation process can be tuned by slight perturbation of experimental conditions.

In our group we study the aggregation properties of conformationally-constrained peptides with two principal aims:

1. To fix the physico-chemical parameters triggering the growth of supramolecular aggregates and, by hierarchical self-assembly) determining the morphology of the supramolecular structures at nanometric and mesoscopic scale. In this connection, the study of peptide aggregation may give important insights on the evolution of several neurodegenerative diseases and precious information for the design of new molecules with pharmacological properties (Fig. 1a).
2. To engineer the surface properties of solid substrates on the nanoscale, producing hybrid biomaterials. Peptide films can be immobilized on surface by covalent self-assembly (self-assembled monolayers) and by Langmuir-Blodgett techniques, allowing us to control the film thickness, morphology and molecular composition (Fig. 1b).

Peptide films can be used as biocompatible platforms for catalysis, optoelectronic and biomedical applications (tissue engineering, protein sensing, biomineralization). (1-6)

In this contribution, we will report on the design, characterization and properties of selected 2D and 3D bio-inspired materials and highlight their potential for applications in biomedicine and optoelectronic devices. Examples include supramolecular peptide aggregates and helical peptide-modified surfaces able to generate current under light illumination.

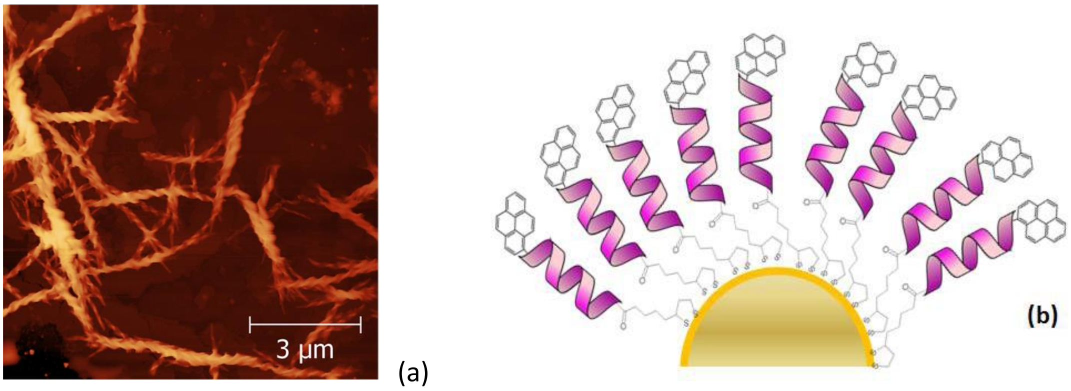

Figure 1. (a) Peptide fibers obtained by self-assembly of conformationally-constrained oligopeptides; (b) Titanium/gold nanoparticles functionalized by optically-active peptides constituting the harvesting unit of a dye-sensitized solar cell.

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Characterization of Lanreotide Autogel using combination of imaging and magic angle spinning NMR spectroscopy with atomic force microscopy

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Lanreotide Autogel(®) (ATG) [Somatuline(®) Autogel(®), Somatuline(®) Depot(®)] is a prolonged-release, supersaturated aqueous gel formulation of the somatostatin analogue lanreotide acetate that acts via somatostatin receptors to reduce both growth hormone and insulin-like growth factor-I levels. It is a valuable option in the treatment of acromegaly, with potential advantages being ease of administration and longer dosing intervals in patients who have an adequate response to initial therapy. Lanreotide ATG also has the advantage of being available in a convenient pre-filled syringe and is given subcutaneously rather than intramuscularly.

In the present contribution we report the use of the pulsed field gradient (PFG) diffusion ordered spectroscopy (DOSY) Magic angle spinning NMR to characterize the supramolecular self-assembly and molecular mobility of different sample of Somatuline auto gel prepared according to different synthetic procedures. Diffusion coefficient, was used to calculated the hydrodynamic ray of supramolecular assembly and to build relative molecular model. DOSY data were integrated with NMR imaging measurements and Atomic force microscopy imaging.

WS3 PO06

N-glucosylated peptide conjugates for an antigen-specific immunotherapy of multiple sclerosis

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Antigen-specific immunotherapy is urgently needed for disease-specific treatments of most autoimmune and rheumatic diseases. The main goal is to remove autoreactive cells and antibodies and/or induce immune tolerance to self-antigens aberrantly modified. Multiple Sclerosis (MS) is a neurodegenerative disease presumably involving an antibody-mediated mechanism in the damage of myelin sheath surrounding the axons in the central nervous system. Since the aetiology is still unknown and the current therapies are feeble, isolating the specific autoantibodies is crucial to understand and treat this complex pathology. We recently demonstrated that a set of defined asparagine-linked glucosyl moieties (up to 9) in adhesin proteins, expressed by the emerging pathogen non-typeable Haemophilus influenzae, is crucial to recognize high-affinity IgM antibodies in a disease form of MS. This result is the first instance that exposure to infectious agents may be associated with increased MS risk and progression and linked to exogenous, bacterially-derived, antigens mimicking mammalian cell surface glycoconjugates triggering autoimmune responses in MS. (1)

With the idea in mind that circulating IgMs are perpetuating a non-self recognition of CNS myelin triggering MS disease activity, we developed a collection of synthetic N-glucosylated adhesin peptides to correlate 3D structure with IgM antibody titre. Short unstructured N-Glc peptides displaying the highest IgM affinity (IC_{50} 10^{-10}-10^{-8}) were selected to load onto different polymeric scaffolds to obtain an octopus-like N-Glc-adhesin dendrimer ideally trapping serum IgMs. Indeed, the achievement of synthetically accessible, antigen-decorated microarchitectures is a promising stratagem for the purification and characterization of specific IgMs. This unmet need in chemical immunology, has the final aim to set up a selective apheresis technology for a personalized MS treatment with a clear industrial potential exploitation.

References: 1. M. T. C. Walvoort, C. Testa et al., Scientific Reports, 2016, 6: 39430

WS3 PO07

Peptlab@UCP: a prototype platform for cGMP large scale peptide synthesis to favour phase I and II clinical studies

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Peptlab@UCP is an R&D platform characterized by a strong know-how in chemical biology, organic chemistry, synthesis, purification and analysis of peptides and proteins. Since 2009, aim of Peptlab@UCP is to develop its activity in the field of active pharmaceutical ingredients (API), diagnostics, cosmetics, food and cultural heritage. This was made possible thanks to the "*Chaire d'Excellence"* ANR-09-CEXC-013-01 (2009-2013) funded by the "Agence Nationale de la Recherche" of the French Ministry of Education and Research.

In order to decrease the costs of large-scale production of peptides as API for phase I and II clinical studies, the Université Paris-Seine in collaboration with CEM (Charlottesville, VA, USA), and with the financial support of "Region Ile de France", launched the first **KiloPeptLab@UCP cGMP unit** to support SMEs with peptides in their pipeline, to develop their business. Equipment in this unit is able to produce up to 1 Kg peptide per batch under microwave irradiations by solid-phase synthetic strategies under cGMP conditions.

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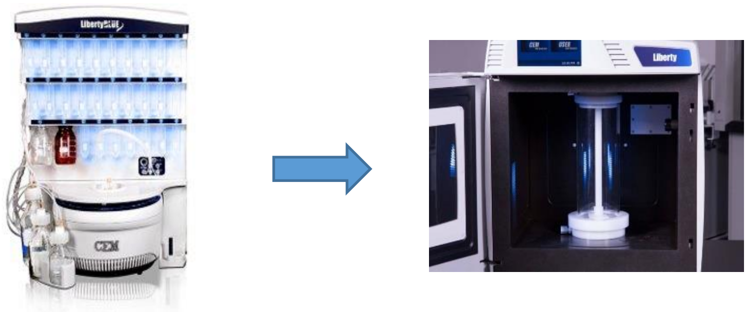

The LibertyBlue™ and the LibertyPro™ from CEM have been chosen to scale up peptides as API. The scalability and the high purity synthesis have been demonstrated on several peptide sequences. This strategy reduces development costs and optimization times increasing speed of production (1).

References: 1. Large Scale Peptide Production Via Microwave Assisted Solid Phase Peptide Synthesis (SPPS) _ Keith A. Porter and Jonathan M. Collins, CEM Corporation, Matthews, NC 28106, USA.

WS3 PO08

Novel decameric peptide of *Spirulina platensis* with potent *in vivo* antihypertensive activity

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Arthrospira Platensis, better known as "Spirulina" is the top-sell product in the nutraceutical market. This blue-green microalga possesses exceptional nutritional properties, in particular a high protein content (1).

While numerous scientific evidences point out the healthy properties of peptides deriving from the protein fraction of this microalga little is known about the bioavailability of the resulting peptides after ingestion, and hence, their bioactivity is far from be unveiled. To highlight these questions, in this work the protein fraction of Spirulina was subjected to in vitro simulated gastro-intestinal digestion, and the resulting digest was characterized by a multi-step peptidomic workflow based on the combination of untargeted and targeted mass spectrometry methods. A novel decameric peptide was identified which exerted direct endothelium-dependent vasodilation of ex vivo vessels, an effect occurring via a PI3K/AKT pathway converging on NO release. In vivo, administration of SP6 evoked a significant hemodynamic effect, reducing blood pressure, an action absents in eNOS (endothelial nitric oxide synthase)-deficient mice. Finally, in an experimental model of arterial hypertension, SP6 exerted an antihypertensive effect, improving endothelial vasorelaxation associated with enhanced serum nitrite levels (2). Based on our results, this novel decameric peptide may extend the possible fields of therapeutical application for spirulina-derived peptides.

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WS4 - CHEMISTRY MEETS LIGHT: APPLICATIONS AND PERSPECTIVES IN THE FIELDS OF ENERGY, ENVIRONMENT, HEALTH, NANOTECHNOLOGY, FOOD AND CULTURAL HERITAGE

The workshop aims at presenting and discussing, with an interdisciplinary approach, the contribution of Photochemistry to various applicative and societal fields.
In particular, it will deal with (a) conversion of solar energy in heat, electricity and fuels; (b) water remediation and air purification by means of photocatalysts; (c) use of photochemical processes to obtain chemical products in innovative and sustainable ways; (d) development of photoactive molecular species for medical diagnostics and therapy; (e) design and synthesis of photoactive nanomaterials, molecular devices and machines to be used in various fields, from information technology to medical diagnostics and therapy; (f) preparation of new and safer dyes, additives, and preservatives for food; (g) use of photochemical techniques for the conservation and restoration of cultural heritage.
The workshop will also address the problem of ethically correct uses of Photochemistry for a safe and sustainable technological and societal development.

WS4 - Organizing Committee and Conveners

- Alberto Credi, University of Bologna, Italy;
- Margherita Venturi, University of Bologna, Italy;
- A. Prasanna de Silva, Queen's University of Belfast, Northern Ireland;
- Andrea Peluso, University of Salerno, Italy.

WS4 – Invited and Keynote Lectures

- **WS4 IL01** – A. Prasanna de Silva, Queen's University Belfast, "*Fluorescent sensing and logic systems".*
- **WS4 KN01** – Françisco Raymo, University of Miami, "*Photoswitchable Fluorophores for Bioimaging Applications*".
- **WS4 KN02** –Serena Silvi, University of Bologna, "*Molecular devices and machines: challenges and perspectives".*
- **WS4 KN03** – Licheng Sun, KTH Royal Institute of Technology Stockholm, "*Water splitting for solar fuels - From natural to artificial photosynthesis".*
- **WS4 KN04** – Aldo Di Carlo, University of Roma, "*2D Materials for perovskite photovoltaics: from graphene to MXenes".*
- **WS4 KN05** – Timothy Noël, University of Eindhoven, "*Solar photochemistry coming of age? – The development of luminescent solar concentrator-based photomicroreactors".*
- **WS4 KN06** – Stefano Protti, University of Pavia, "*Photoinduced sustainable arylations".*
- **WS4 KN07** – Simona Ghiani, Bracco Imaging SPA, *"Dye-based imaging probes for contrast-enhanced imaging applications".*
- **WS4 KN08** – Engin U. Akkaya, Dalian University of Technology, "*Recent progress in the chemistry of photodynamic therapy".*
- **WS4 KN09** – Aldo Romani, University of Perugia, "*Is the light only harmful to artworks?"*

WS4 IL01

Fluorescent Sensing and Logic Systems

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One of the main principles underlying fluorescent sensors is based on PET (photoinduced electron transfer),[1] according to which a switching 'on' of fluorescence in response to chemical analytes can be designed. Since its generalization in Colombo, Sri Lanka, it has now grown to involve over 530 laboratories around the world. Some of these sensor systems are serving in critical care units in hospitals and in ambulances, performing blood diagnostics. These form the basis of a half-billion dollar industry.[2] Other sensors visualize intracellular players. Yet others map species distributions in nanometric spaces near membranes.[3] These spaces are too small for the tiniest silicon-based electronic devices to enter. Our introduction of molecular logic gates[4,5] from Belfast, Northern Ireland, allows us to build more complex sensors and micro-object identification systems. More complex operations involving sequential logic[6] and even human-scale computations, e.g. edge detection of objects[7] and outline drawing (Figure 1),[8] are now achieved by molecular systems. More than 820 laboratories have contributed to this field so far.

A short video on this topic is available at www.youtube.com/watch?v=sLGnZDP5Ecg

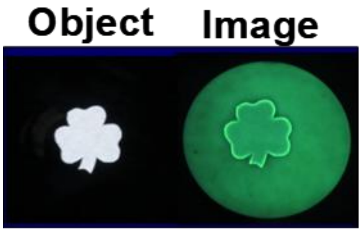

Figure 1. Outline drawing image of an object achieved by a molecular system.

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WS4 KN01

Photoswitchable Fluorophores for Bioimaging Applications

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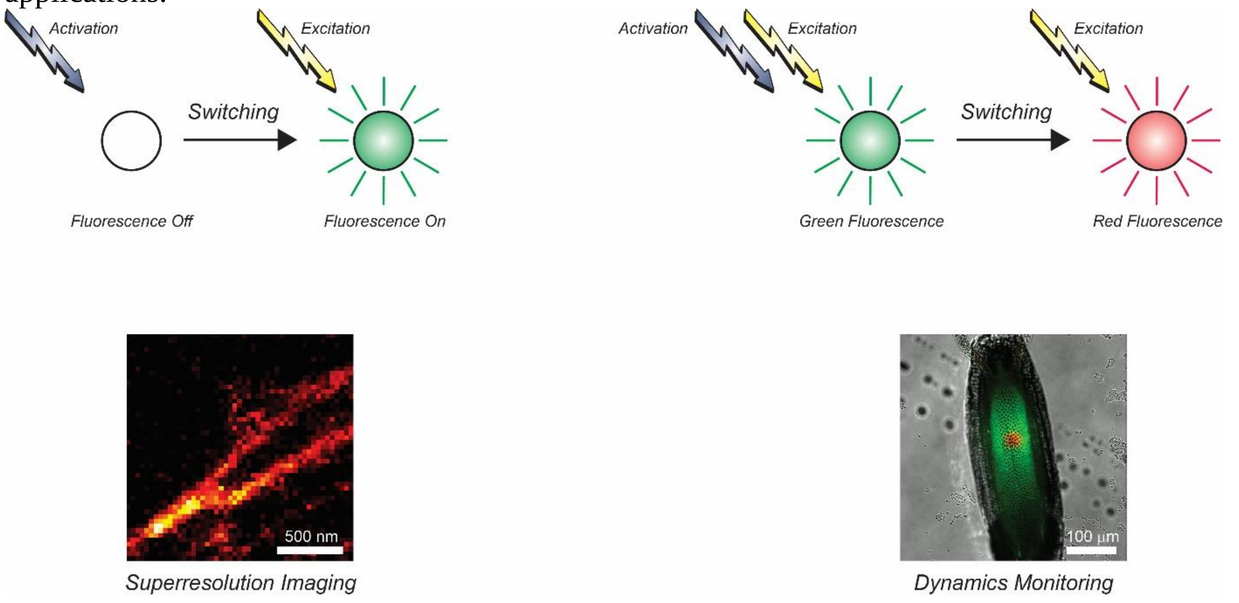
The goal of our research program is the development of operating principles to switch fluorescence under the influence of external stimulations.[1] We design molecules capable of switching from a nonemissive to an emissive state, upon illumination at an appropriate activation wavelength and then produce fluorescence after irradiation at a given excitation wavelength. The resulting compounds permit the confinement of fluorescence within a defined region of space at a specific interval of time, relying exclusively on the interplay of beams illuminating the sample at the activation and excitation wavelengths. Such level of spatiotemporal control offers the opportunity to overcome diffraction and reconstruct fluorescence images with spatial resolution at the nanoscale. We also design molecules capable of interconverting between emissive states with spectrally-resolved fluorescence, upon illumination at an appropriate activation wavelength. The resulting compounds allow the switching of the fluorescence color with spatiotemporal control in a given sample of interest and the subsequent monitoring of dynamic events in real time with the sequential acquisition of fluorescence images. We are particularly interested in exploring these operating principles for fluorescence switching to visualize intracellular substructures with nanometer resolution as well as track the translocation of species within living organisms. Thus, our fundamental investigations on molecular switches can eventually lead to the realization of innovative imaging probes for a diversity of bioanalytical applications.



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WS4 KN02

Molecular devices and machines: challenges and perspectives

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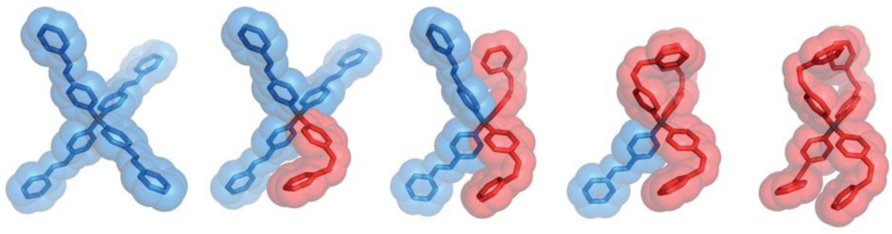
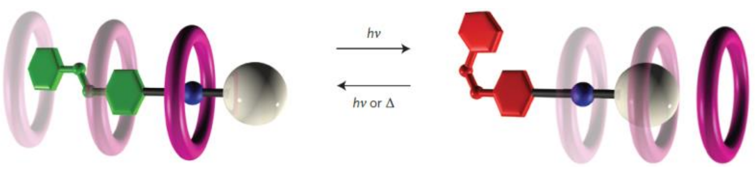
The bottom-up design, construction and operation of artificial mechanical devices and machines on the molecular scale is a topic of great interest in nanoscience and a fascinating challenge of nanotechnology, which has stimulated the creativity of chemists in the past three decades (1). The realization that the material base of life is based on a formidable array of natural nanomachines is responsible for much of the stimulus to develop artificial analogues. To enable the transition of artificial molecular devices from simple laboratory curiosities to key components of novel technologies, they must be interfaced with the macroscopic world, principally in relation to energy supply and information exchange: light is an ideal tool to fulfill both requirements. We will describe here some recent investigations undertaken in our laboratory on photoactive molecular and supramolecular architectures. The reversible photoisomerization of molecular crystals based on star-shaped azobenzene tetramers (2) and the directional and autonomous movement of artificial supramolecular pumps based on interlocked structures (3) will be described.

Star-shaped azobenzene tetramers



An artificial supramolecular pump



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WS4 KN03

Water Splitting for Solar Fuels—From Natural to Artificial Photosynthesis

Licheng Sun

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Nature uses solar light and water to drive chemical reactions in biological systems, and understanding the mechanism of water splitting by the Mn4CaO5 cluster in oxygen envolving complex (OEC) of Photosystem II is essential for the design of highly efficient synthetic catalysts for artificial photosynthesis. In this lecture, I will start to summarize the great efforts having been made during the past decades on the studies of water oxidation mechanisms in OEC and synthetic molecular water oxidation catalysts such as Ru(bda) series: the water nucleophilic attack to a Mn(V)=O species and Oxo-oxyl radical coupling pathway. Based on most important experimental results reported in the literature and our own understandings, I will show a new mechanism of water splitting in OEC with a full catalytic cycle. To approve this new proposal, we have synthesized a Mn oxides based water oxidation catalyst. Through electrochemical study and infrared spectroscopic investigation, we could demonstrate a catalytic cycle of water oxidation by this Mn oxides with similar mechanism of O-O bond formation as shown in OEC of Photosystem II.

As one of applications of water splitting for solar fuels, the use of water as an oxygen and hydrogen source for oxygenation and hydrogenation of organic substrates to produce valuable chemicals is of utmost importance as a means of establishing green chemical syntheses. A paired electrosynthesis cell for the respective oxygenation and hydrogenation of organic compounds, with water as both the oxygen and hydrogen source will be discussed during this lecture. Conversions efficiencies and selectivities of ≥99% were achieved during the oxygenation of 5-hydroxymethylfurfural (HMF) to 2,5-furandicarboxylic acid (FDCA) and the simultaneous hydrogenation of *p*-nitrophenol to *p*-aminophenol. This paired electrosynthesis cell has also been coupled to a solar cell as a stand-alone reactor in response to sunlight.

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WS4 KN04

2D materials for perovskite photovoltaics: from Graphene to MXenes

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Halide Perovskite such as $CH_3NH_3PbI_3$ (MAPI) have opened up new directions to fabricate cost effective and highly efficient optoelectronic devices and in particular solution process solar cells. Many factors can influence the efficiency and stability characteristics of Perovskite Solar Cells (PSCs). In particular, interfaces can impact on efficiency, stability, layers deposition, charge recombinations and compound intermixing/diffusion. In this perspective, bidimensional (2D) nanomaterials, such as graphene and related materials can play a primary role owing to their 2D nature and the large variety of 2D crystals, whose complementary opto/electronic properties, can be on-demand tuned by chemical functionalization and edge modification. The so-called Graphene Interface Engineering (GIE) has shown to be extremely effective in PSC technology both at lab cells (small area) level and at large area (module) level. We demonstrate the use of graphene and 2D materials as an effective way to control the morphology [1] and to improve stability and efficiency [2,3]. By dispersing graphene flakes into the mesoporous TiO2 layer and by inserting graphene oxide (GO) as interlayer between perovskite and Spiro-OMeTAD layers, we demonstrate a PCE exceeding 18% with a two-step MAPI deposition, carried out in air.[2] Further optimization of the 2D interface layers could promote the efficiency to 20%[4] with a strong improvement of the stability. Recently MXenes (MX) came out as a new class of 2D materials with outstanding properties such as high electronic conductivity, hydrophilic surface, high surface energy, and remarkable tunability in term of work function, ranging from 1.6eV till 6.5eV. We demonstrated the use of MX for perovskite photovoltaics by fine tuning the interface properties in engineered mesoscopic device. In particular, we modified the photo-electrode properties by adding MX within the precursor solutions. UPS measurements showed a shift in perovskite workfunction testifying the role of MX in modifying the perovskite electronic structure. The proposed MX-perovskite cells showed superior PCE overcoming 20% with outstanding reduction of hysteresis phenomenon. Detailed DFT calculations and device simulations permitted to define the role of MX. The proposed 2D-Perovskite approaches have been exploited for the fabrication of state-of-the-art large area perovskite modules with a PCE > 15% (active area exceeding 80 cm^2) paving the way to an industrialization phase compatible with standard fabrication processes [5].

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WS4 KN05

Solar photochemistry coming of age? – The development of Luminescent Solar Concentrator-based Photomicroreactors

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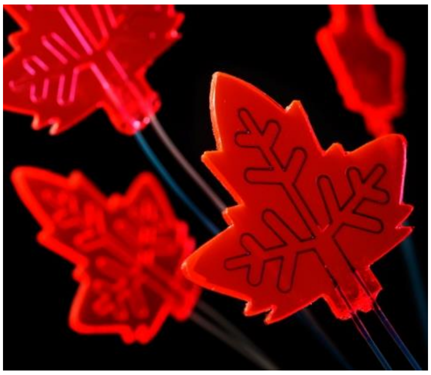
Visible light photoredox catalysis has received much attention in recent years as a mild and sustainable activation mode for organic molecules.[1] In particular, when coupled with microreactor technology, an efficient irradiation of the reaction media is achieved.[2] Yet, the use of solar energy to promote visible light mediated reactions is not widespread and adopts energy-inefficient systems like the "flask in the sun". The efficient use of solar light as perennial energy source in the fine chemical production industry can reduce the dependence on fossil fuels and enable the transition toward a world driven by clean energy.[3]

In this lecture, we will discuss a novel device integrating the luminescent solar concentrator (LSC) concept with photomicroreactors, allowing the direct use of solar light in photochemistry without the need for any intermediate energy conversion.[4] The device is capable of capturing direct and diffuse sunlight, converting it into a narrow wavelength and delivering it to the embedded microchannels (See Figure).[5]



The performance of the device was studied both in indoor and outdoor conditions, significantly outperforming the non-dye-doped device.[6,7] We believe that our strategy to merge flow photochemistry and luminescent solar concentrators represents a departure from the use of traditional solar photoreactors combined with reflectors, photovoltaic cells and solar tracking modules. Also, we anticipate that the design will be applicable to other photochemical transformations, ultimately delivering a powerful tool for the sustainable and solar-driven continuous manufacturing of valuable chemical compounds, such as pharmaceuticals, agrochemicals and solar fuels.[8]

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WS4 KN06

Photoinduced Sustainable Arylations

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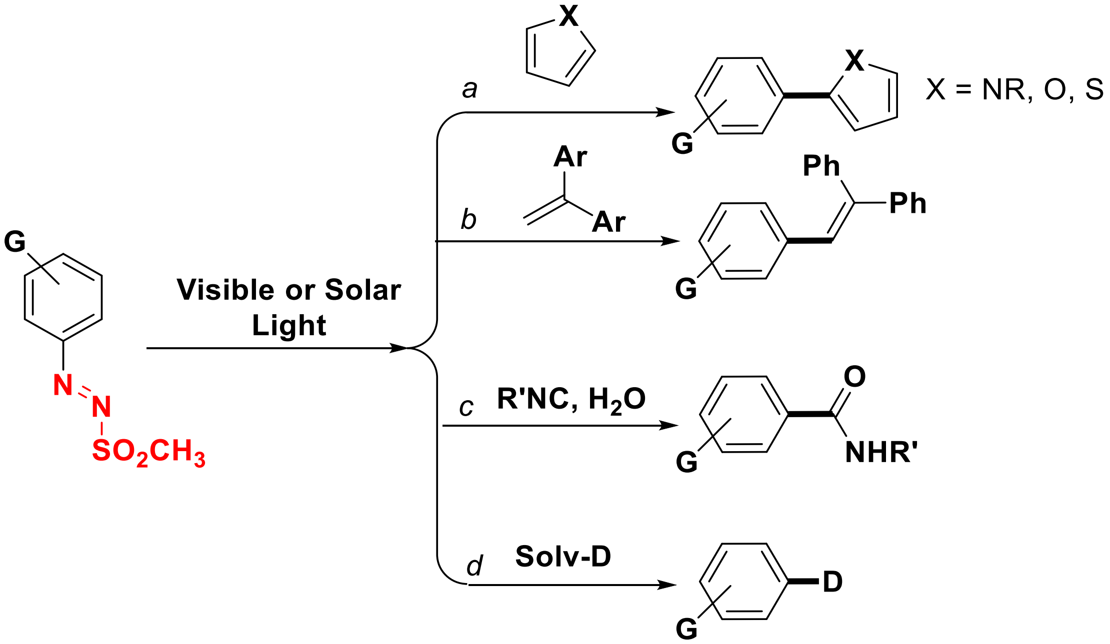
In the recent decade the demand for synthetic protocols that proceed under mild and metal-free conditions has become urgent. Indeed, the risk of contamination of the end products by transition metals (even in trace) is a serious drawback for pharmaceutical and cosmetic applications.[1]
Arylazo sulfones are bench-stable and easily prepared compounds that can be easily prepared from commercially available colorless anilines in two steps.[2] Such derivatives bear a -$N_2SO_2CH_3$ moiety (dubbed as *dyedauxiliary* group) able to impart both color and photoreactivity to the molecule. Thus, arylazo sulfones can generate aryl radicals (via homolytic cleavage of the N–S bond) and triplet aryl cations (in turn obtained via N-S bond heterolysis) in a wavelength-selective fashion, under irradiation with visible and UV light, respectively; obviously, upon sunlight esposition both species are released.[2] In the last years the photoreactivity of this compounds has been exploited by our group in a wide range of synthetic protocols for the preparation of (hetero)biaryls (scheme 1, path a) ,[2] allyl- and vinylarenes (path b),[3] aromatic amides (path c)[4] as well as of deuterated arenes (path d)[5]. Notably, the presented processes take place under metal- and photocatalyst- free conditions, and only visible (or solar) light is needed to activate the substrates.



Scheme 1

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WS4 KN07

Dye-based imaging probes for contrast-enhanced imaging applications

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Among several techniques that have being used for imaging and diagnosis of cancer tissues, imaging based on optical probes, such as near-infrared (NIR) fluorescence imaging is gaining attention in the diagnostic field mainly due to the high sensitivity of this technique and relatively low cost.

In particular, NIR fluorescence-guided surgery is gaining relevance in the field of surgical oncology to guide tumor resection; this technique takes advantage of fluorescent probes signal accumulation within the tumor, making surgical procedures more efficient in identifying tumor vs healthy tissue, with consequent reduction of tumor recurrences.

It is noteworthy that the development of a suitable NIR fluorophore is a long and difficult process since it must satisfy several chemical, and biological requirements, and even if several advancements have been made so far, only few of them have been approved for clinical use, such as Indocyanine Green (ICG), for restricted clinical applications. Thus, there is a need for the design of new class of dyes with improved optical, stability and targeting properties.

The aim of this talk is to report a series of examples of novel optical probes designed with appropriate optical and targeting properties for the real-time visualization of cancerous lesions during open-air or endoscopic surgical treatments by NIR fluorescent imaging. Different pre-clinical studies dealing with small molecules, designed by linking a fluorescent probe and an appropriate molecular vector (1) or with nano-size probes aimed to exploit a combination of molecular targeting and passive accumulation mechanisms will be presented.

Among different fluorescent probes, nanoparticles (NPs) loaded with ICG showed interesting and versatile properties. Actually, due to its amphiphilic properties, ICG is characterized by high not specific binding to plasma proteins and by a short plasma half-life in humans that prevent any efficient uptake of the probe in pathological tissues. Instead, the use of NPs has been proposed for ICG delivery (2) in order to enlarge ICG applicability as NIR fluorescent probe for tumor targeting and to improve its *in vivo* stability (Figure 1).

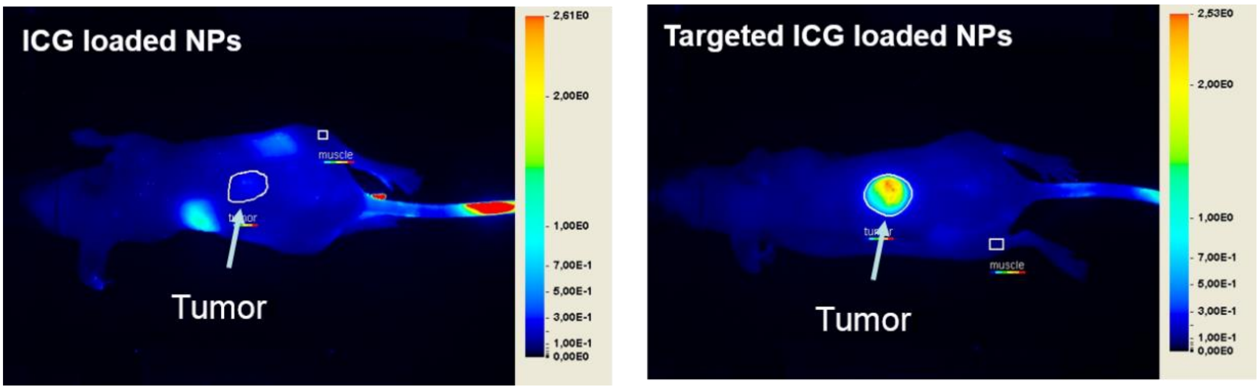

Figure 1. Example of ICG loaded NPs for tumor targeting in NIR fluorescence imaging

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WS4 KN08

Recent Progress in the Chemistry of Photodynamic Therapy

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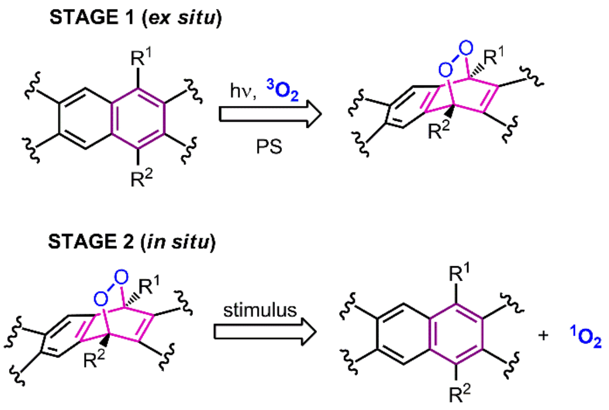
Photodynamic therapy (PDT) of cancer has been considered a promising therapeutic approach for decades. Principal requirements for photodynamic action were established by the experiments of Raab and von Tappeiner at the turn of the 20th century. Based on their work, which was followed up by many others, a photosensitizer that can be excited by light in the visible, but more preferably in the red or near-IR region of the spectrum could sensitize ground state molecular oxygen and generate a short-lived, cytotoxic reactive oxygen species, singlet oxygen. This process is inherently regioselective, as the singlet-oxygen generation will take place only in the region at which the light beam is directed. In combination with the enhanced permeation and retention (EPR) effect, which leads to sensitizer accumulation in tumors, this non-invasive, or minimally invasive, treatment protocol, with tolerable side effects and a bonus of enhanced immune response, has tremendous therapeutic potential. However, the full promise of PDT has not been realized except perhaps for some niche applications such as superficial lesions. The limited applicability is not necessarily due to the lack of optimal sensitizers or smart delivery/activation processes; the problem unfortunately lies at the core of the PDT paradigm. First, even at the optimum wavelengths, the tissue penetration of light is very ineffective beyond the first few millimeters. The second issue is oxygen concentration. Most tumors develop a hypoxic region, and this is more common in aggressive metastatic tumors. Such hypoxic tissues are highly resistant to chemotherapy and radiotherapy

In our research group, we have been trying to address these two fundamental problems by separating photonic excitation from the actual delivery of the singlet oxygen, in a two-stage plan for photodynamic action.[1-3] This requires the development of stable storage compounds, which could then be transferred to the biological target, and later, release its cargo, on cue. The most promising class of such storage compounds are endoperoxides derived from arenes. Our recent progress along these lines will be presented.



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WS4 KN09

Is the light only harmful to artworks?

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It is well known that the light is one of the most relevant parameters acting in the modification processes of several materials belonging to the Cultural Heritage artworks' composition. In fact, commonly accepted recommendations for museum lighting practice agree in that ultraviolet (UV) and infrared (IR) radiations should be severely restricted and that exposure to visible light should be limited in both intensity and duration (1). Nevertheless, whatever choice require a compromise between visibility and conservation, then to avoid interaction between artworks and light is impossible. Among the huge number of different materials used in artworks production, the colored ones, namely the dyes and the pigments are the more sensitive to the visible light action and the population of their electronic excited states primes many reactive pathways, regardless the inorganic or organic chemical nature of the subject (2). The role of photochemists become then crucial in order to reach an in-depth understanding of the photochemical processes, providing to the museum professionals a solid framework to develop preventive conservation strategies through the selection of the optimal lighting parameters. But the light can be not only dangerous for the artworks because it also represents a powerful and suitable tool for materials' investigation in a completely not invasive way. Every spectroscopic technique is potentially able to use the light as a probe for the identification of different materials and this not invasive diagnostic approach has become the main analytical protocol in several conservation science laboratories all over the world. Our country has been pioneer in this field creating the first mobile laboratory (3), called MOLAB®, which is nowadays fundamental part of the rising E-RIHS, the European Research Infrastructure for Heritage Science. Since its birth in 2004, MOLAB® has brought "the light" of its instrumentations all around the Europe, introducing new analytical methods and devices and working on monuments, stained glasses, illuminated manuscripts, paintings and many other artworks. The large experience growth during the years has allowed the contribution of MOLAB's operators to the development of new materials and new scientific instrumentations. Over these years, we have learned to use light to admire works of art not only with our eyes, promoters of the emotions that artworks provide, but also with technological eyes, sensitive to the whole electromagnetic spectrum and able to reveal the complex chemical mystery that these precious objects contain.

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WS4 - Oral Communications

- **WS4 OR01** – Chao-Yi *Yao “Molecular computational identification (MCID) of small objects in populations”*
- **WS4 OR02** – Erica Paltrinieri *“Light effected autonomous molecular pumps”*
- **WS4 OR03** – Sara Gullace *“Characterization of novel nanostructured gold counter electrodes for dye sensitized solar cells”*
- **WS4 OR04** – Bibhuti Bhushan Show *“Electrochemical synthesis of oxide and sulphide semiconductor thin films: their characterizations and applications”*
- **WS4 KN05** – Timothy Noël *“Solar photochemistry coming of age? – The development of luminescent solar concentrator-based photomicroreactors”*
- **WS4 KN06** – Stefano Protti *“Photoinduced sustainable arylations”*
- **WS4 OR05** – Roberto Comparelli *“Visible light active nanocrystalline photocatalysts for environmental applications”*
- **WS4 OR06** – Andrea Pucci *“NIR Reflective surfaces based on organic coatings”*

WS4 OR01

Molecular Computational Identification (MCID) of Small objects in Populations

Chao-Yi Yao[a], *Jue Ling*[a], *Sheenagh M. Weir*[a], *Bernadine O. F. McKinney*[a], *Gareth J. Brown*[a], *Linyihong Chen*[a], *A. Prasanna de Silva*[a]

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Semiconductor electronic technology increasingly impacts on our lives. One of these impacts is via radiofrequency identification (RFID) (1). However, RFID technology can only operate on objects which are larger than 0.1 mm because of limits on the size of antennas for receiving and transmitting radio signals. This means that individual biological cells involved in cell diagnostics and polymer particles in combinatorial chemistry lie outside the scope of RFID technology. Molecular logic-based computation (2-4) can handle such problems because sub-nanometric molecules can easily receive and transmit light signals. While fluorescent molecular tags can provide individual ID's for about 100 objects (5), much larger populations should be addressable if the tags show additional input-output responses of the Boolean logical sort (6, 7). Besides fluorescence excitation and emission wavelengths, new parameters such as the nature of input, logic type of output response and output switching threshold become available. Additional diversity could be introduced by double-tagging of objects which also brings in multi-valued logic to the chemical sphere.

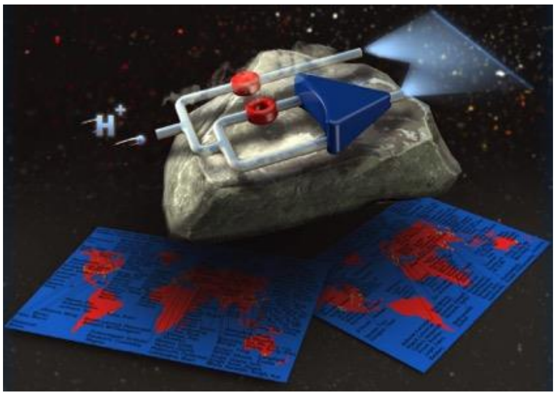

Figure 1. Artist's impression of molecular logic tag connected to small solid object.

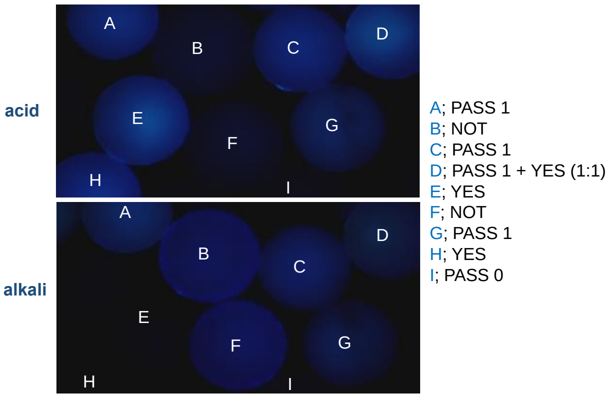

Figure 2. Fluorescence micrographs of molecular logic tagged beads in acid and alkali.

Figures 1 and 2 show schematically and experimentally, respectively, how the above ideas are brought to reality. It is clear that parking fluorescent molecular logic gates of various types on small inorganic or organic objects and exposing them to a wash-and-watch protocol allows their visual distinction. Mechanistically, a YES gate concerns the input species stopping a photoinduced electron transfer (PET)(8) which was previously occurring from a receptor component to the fluorescent unit so that the quenched emission is now switched 'on'. NOT gates have PET processes being launched by the input species whereas PASS 1 gates have no PET at all.

We acknowledge the support of the China Scholarship Council and the Department of Employment and Learning of Northern Ireland.

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WS4 OR02

Light Effected Autonomous Molecular Pumps

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Movement is one of the central attributes of life, and a key feature in many technological processes (1). Macroscopic engines produce motion through combustion or electrical energy, while movement in living organisms is produced by machines and motors of molecular size that typically exploit the energy of chemical fuels at ambient temperature to generate forces and ultimately execute functions. A molecular machine can be defined as "an assembly of a discrete number of molecular components that exhibit mechanical movements in response to an external stimulus" (1). Molecular machines are present in all living organisms, where they perform essential tasks encompassing movement and locomotion, energy conversion, transport and regulating functions. The energy input used to produce motion is the most important characteristic of molecular machines. Although all living organisms rely on sunlight as the primary energy source, nearly all types of biomolecular machines are powered by chemical 'fuels' that allow a convenient storage, transport and delivery of energy (2). The use of light to power artificial molecular machines, however, is preferable with respect to chemical fuels, as it relies on reversible and clean photochemical reactions. Moreover, an appropriate tuning of the light source can lead to targeted structural changes in molecular systems.

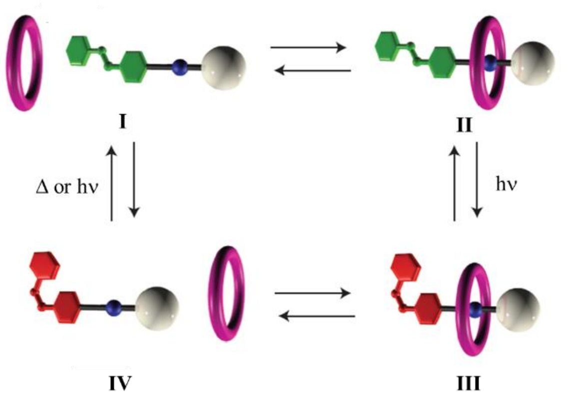

Figure 1. Photoinduced unidirectional transit of a molecular ring along a molecular axle.

As an example, molecules containing azobenzene units (composed of an RN=NR double bond) are photoisomerised from the E isomer to the corresponding Z isomer by irradiation around 320-380 nm (3). Our group recently reported the first example of artificial molecular pump activated by light by combining the *E*/*Z* photoisomerization of azobenzene to the self-assembly of a pseudorotaxane. Such system is composed of a macrocycle and a molecular axle containing an ammonium functionality, the *E*-azobenzene unit, and a pseudo-stopper (Figure 1). At first, the ring threads through the favoured *E*-azobenzene side, and interacts with the ammonium station, providing the complex **I**. Photoisomerisation of the azobenzene then leads to the high-energy complex **III**, in which the dethreading of the ring through the pseudo-stopper end is favoured due to the variation in the kinetic barriers. Finally, re-isomerisation *Z*/*E* of the azobenzene closes the cycle (4). In such a way, an autonomous and unidirectional pumping driven by light is achieved, that paves the way towards the construction of artificial molecular systems to be used as directional transmembrane transporters. Financial support from the EU (H2020 ERC AdG "Leaps" no. 692981) is gratefully acknowledged.

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WS4 OR03

Characterization of novel nanostructured gold counter electrodes for dye sensitized solar cells

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Over the last two decades, the research in the Dye Sensitized Solar Cells (DSSCs) field has been mainly focused on the seek for iodine-free electrolytes and, thus, for Pt-free counter electrodes (CEs). Conventionally, DSSC counter electrodes are Pt-based, but despite its fundamental contribution to the overall efficiency of the solar cell, Pt has limited long term stability other than being rare and expensive.(**1,2**) Generally, the conventional platinum CEs show poor catalytic activity towards iodine-free redox couples, thus resulting in relatively moderate power conversion efficiency. (**3**)
The aim of our work is to develop, study and characterize novel nanostructured gold CEs to supersede the catalytic activity of platinum towards iodine-free redox mediators. The counter electrodes preparation by pulsed laser ablation (PLA) and morphology will be discussed, as well as their activity as catalysts towards the $Co(bpy\text{-}pz)_2^{2+/3+}$ redox process by means of voltammetric analysis and current-voltage measurements in symmetrical dummy cells. Furthermore, their behaviour in fully-assembled solar cells (Y123 sensitized TiO_2 photoanode ‖ $Co(bpy\text{-}pz)_2^{2+/3+}$ redox mediator ‖ gold nanostructured CE) will be presented. (**4**)
PLA is a promising way to fabricate transparent and high performance Pt-free electrodes for future large-scale applications not only in photovoltaics but even for others devices employing gold for catalysis, sensing, opto-electronics.

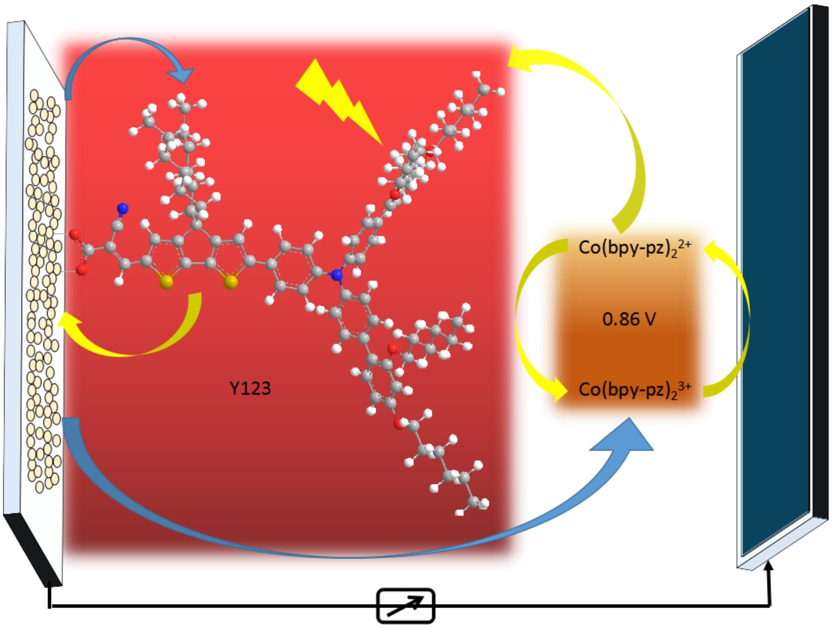

Fig. 1. Schematic representation of the studied dye-sensitized solar cells.

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WS4 OR04

Electrochemical synthesis of oxide and sulphide semiconductor thin films: their characterizations and applications

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Semiconducting materials, mainly in the form of thin films, have immense importance in present day science and technology. We can find vast applications of semiconducting materials in solar photovoltaic cells, sensors, radar technology, and infrared cameras for night vision, lasers, several electronic devices like diodes, transistors, memory storage devices etc. Polycrystalline thin films are prepared mainly by physical, chemical and electrochemical techniques. The beauty of electrochemical process lies in its simplicity, and of course, in its cost effectiveness. Here, the author has specifically aimed to develop some important materials like CuO, α-Fe_2O_3, FeS, FeS_2, SnS, Cu_2ZnSnS_4 etc by applying both the two electrode galvanic technique and the three electrode electrochemical techniques, to obtain semiconducting films which are prepared in an eco-friendly manner and are reproducible as well as commercially viable. The morphology, composition, and optical properties were characterized by XRD, FESEM, HRTEM, UV-Vis, Photoluminescence, Raman, FT-IR, EPR and electrical measurements by two and four probe I-V techniques. They were also found to be applicable either as photocatalysts, electrocatalysts or as materials for photoelectrochemical (PEC) solar cells. The development of a facile and green chemical route for the preparation of a well crystallized and stable electrode material still remains a challenge for the fabrication of solid-solid/solid-liquid junction devices.

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WS4 OR05

Visible light active nanocrystalline photocatalysts for environmental applications

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Nanostructured materials exhibit outstanding size/shape dependent properties that make them extremely promising in several application fields. The urgent environmental issues such as water and air pollution have focused increasing efforts in developing photoactive nanoparticles, especially nanosized TiO_2, with the goal to achieve the complete mineralization of pollutants by means of the well-known photocatalytic generation of reactive oxygen species (ROS)[1].

TiO_2 is wide band gap semiconductor, therefore it can be activated only by UV light, thus limiting the fraction of solar spectrum able to generate •OH to ~4%[2]. Current efforts in the field of designing and synthesis of photocatalysts aim at improving charge separation, inhibiting charge carrier recombination and enhancing the catalytic activity in the visible region. To achieve such goals we synthesized, several visible light active TiO_2-based heterostructures photocatalysts, consisting of TiO_2 nanocrystals of different size and shape, rationally modified with noble metals (TiO_2/Ag[3], TiO_2/Au[4], TiO_2/Fe_yO_x/Ag[5]) or carbon nanotubes (TiO_2/CNTs[6-7]) by exploiting several preparation routes. The photocatalytic properties of the obtained nanomaterials have been investigated in the photocatalytic degradation of several organic pollutants in comparison with their commercial counterpart. The obtained results were rationalized and related to the optical structural and morphological characterization results of the each heterostructure. Experimental data point out the higher photoactivity of nanosized catalysts, the possibility to shift their photoactivity in the visible range and their viability for several environmental related applications

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WS4 OR06

NIR reflective surfaces based on organic coatings

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Poor attention has been paid so far to the 50% of NIR radiation flux (750-2500 nm), coming from direct, diffused and reflected sun radiation, which contributes to increase the temperature in urban areas. To reduce the increasing demand for energy consumption for air conditioning or to produce cool fabrics, there is a need for NIR reflective pigments and coatings formulation since reflecting the sun's radiation minimizes the amount of energy absorbed by the surface (1). To date, NIR reflectivity is obtained with the use of inorganic pigments such as expensive metal oxides and complexes (2). The key to obtaining innovative cool pigments is instead the production of NIR reflective organic molecules to avoid the inconveniences related to costs, environmental impacts, while maintaining the efficiency and color provided by the current inorganic pigments. This work aims at the preparation of organic coatings containing designed perylene- and naphthalene-bis imides properly functionalized with peripheral moieties able to confer the desired color and NIR reflectivity according to the π-π stacking behavior of the extended conjugated nuclei (3). Notably, different pigment formulations are prepared from commercially available resin dispersions in water and the NIR reflective features of the derived coatings are discussed in terms of the utilized pigments, additives and their content, and compared with those of commercially available inorganic benchmarks.

Acknowledgements
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WS4 - Poster Communications

- **WS4 PO01 -** Claudia Barolo, Nadia Barbero, Andrea Fin, Alessandra Fiorio Pla, Sonja Visentin and Guido Viscardi *"Functional dyes for photoactive materials: from the synthesis to the biomedical applications"*
- **WS4 PO02 -** Federico Bella, Lucia Fagiolari, Alberto Scalia, Matteo Bonomo, Simone Galliano, Andrea Lamberti, Claudia Barolo, Claudio Gerbaldi *"Aqueous Photovoltaics and Integrated Portable Devices: Novel Trends in the Solar Cells Scenario"*
- **WS4 PO03 -** Amalia Velardo, Alessandro Landi, Amedeo Capobianco, and Andrea Peluso *"Rates of Elementary Charge Separation and Charge Recombination Processes in BHJ solar cells"*
- **WS4 PO04 -** Alberto Credi, Sergey A. Denisov, Gediminas Jonusauskas, Marcello La Rosa, Nathan D. McClenaghan *"Designed long-lived luminescence in quantum dot-chromophore conjugates"*
- **WS4 PO05 -** M. Dell'Edera, F. Petronella, T. Sibillano, C. Giannini, A. Agostiano, M. L. Curri, R. Comparelli *"Development of novel deposition strategies of nano-TiO2 onto unconventional substrates for wastewater treatment"*
- **WS4 PO06 -** C.N. Dibenedetto, E. Fanizza, A. Panniello, A. Agostiano, M.L. Curri, M. Striccoli *"Design of colloidal QD dimers towards quantum optical coherence"*
- **WS4 PO07 -** Marianna Diterlizzi, Stefania Zappia, Silvia Destri, Riccardo Po' *"Water-processable blend nanoparticles for sustainable organic solar cells"*
- **WS4 PO08 -** Alessandro Emendato, Antonio Ruggiero, Michele Laus, Federico Ferrarese Lupi, Katia Sparnacci, Finizia Auriemma, Claudio De Rosa, Anna Malafronte *"Block copolymer based hybrid nanocomposite materials for photovoltaic applications"*
- **WS4 PO09 -** R. Giannantonio, F. Matteucci, R. Comparelli, L. Curri, G. Mascolo *"Nanostructured photocatalysts combined with UV radiation for water treatment"*
- **WS4 PO10 -** Alessandro Gradone, Raffaello Mazzaro, Francesco Romano, Vittorio Morandi, Paola Ceroni *"Luminescent Solar Concentrators based on Silicon Nanocrystals"*
- **WS4 PO11 -** Claudia Graiff, Laura Bergamonti, Pier Paolo Lottici, Carlo Bergonzi, Ruggero Bettini, Lisa Elviri *"Design of 3D printed chitosan-TiO2 scaffolds for removal of amoxicillin from wastewater by photodegradation"*
- **WS4 PO12 -** Claudio Imparato, Marzia Fantauzzi, Giuseppina Iervolino, Can Koral, Antonello Andreone, Gerardino D'Errico, Vincenzo Vaiano, Antonella Rossi, Antonio Aronne *"Noble metal-free photocatalytic hydrogen evolution on gel-derived defective TiO2"*
- **WS4 PO13 -** Francesca Mancuso, Barbara Prandi, Giovanna Lippe and Mara Lucia Stecchini *"Pre-slaughter feed restriction beneficially influences gastric digestibility of sea bream (Sparus aurata L.) fillet"*
- **WS4 PO14 -** Luigi Menduti, Alberto Bossi, Serena Arnaboldi, Clara Baldoli, Emanuela Licandro *"Luminescent boron-functionalized benzodithiophenes"*
- **WS4 PO15 -** Federica Menegazzo, Michela Signoretto, Andrea Campostrini, Danny Zanardo, Giuseppe Cruciani, Giorgio Berto, Luca Scappin *"Photocatalysts in the formulation of traditional Venician Marmorino"*
- **WS4 PO16 -** Pier Paolo Prosini, Ivan Fuso Nerini, Mariasole Di Carli, Gabriele Tarquini, Paola Gorini, Livia Della Seta *"Development of high capacity lithium sulphur batteries"*
- **WS4 PO17 -** Andrea Pucci, Pierpaolo Minei, Giuseppe Iasilli, Francesco Picchioni, Giacomo Ruggeri *"New materials for luminescent solar concentrators"*

- **WS4 PO18 -** Diana Sannino, Vincenzo Vaiano *“Environmental Applications and Organic Syntheses in a UVA-LEDs Photocatalytic Fluidized Bed Reactor”*
- **WS4 PO19 -** Martina Ussia, Giusy Curcuruto, Maria Miritello, Vittorio Privitera, Sabrina Carola Carroccio *“Time-saving formulation of Nickel-free 3D graphene for Visible-Light photocatalysis”*
- **WS4 PO20 -** Chao-Yi Yao, Jue Ling, Linyihong Chen, A. Prasanna de Silva *“Population Analysis of Molecular Computational Identification (MCID) of Small Objects and its Extension to the Near Infrared Region”*

WS4 PO01

Functional dyes for photoactive materials: from the synthesis to the biomedical applications

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Functional dyes are nowadays more and more important in the development of light responsive materials. Over the past five years, we have developed several libraries of functional dyes (from UV to Far-Red and finally NIR absorbing dyes) and their related photoactive materials, useful in a wide range of devices covering optoelectronics, i.e.: solar cells (1) and lighting (2), and biomedical applications, i.e.: photodynamic therapy (3), optical imaging (4) and optical sensors (5).

Among the different classes of organic dyes, polymethine (i.e. squaraines and cyanines) dyes deserve to be considered as innovative potential photosensitizers (PSs) due to their numerous advantages. The extension of the central conjugated bridge, as well as, the functionalization of the edge of the chromophores (6), easily allows the design of innovative probes with NIR properties, high absorption coefficient, bright fluorescence and remarkable photostability in organic media.

On the other hand, the stability of these dyes in physiological media for biological investigation is strongly affected by their chemical degradation and self-aggregation phenomena, limiting their applications. The proper scaffold functionalization along with a well-designed incorporation of these dyes in specific matrixes is extremely important to tackle the stability limitations and to preserve the photophysical characteristics from nucleophilic attacks.

The present contribution is focused on the design and synthesis of a series of NIR absorbing polymethine dyes, bearing different groups, to investigate the structure-activity relationship and to determine the substituents effect on the reactive oxygen species (ROS) generation, cellular uptake and photodynamic activity (7). These dyes were encapsulated in nanoparticles (8) or complexed with biomaterials (9) to promote their use in physiological conditions. These complexes have shown excellent optical properties, remarkable photostability, biocompatibility and an efficient cellular internalization.

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WS4 PO02

Aqueous Photovoltaics and Integrated Portable Devices: Novel Trends in the Solar Cells Scenario

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Photovoltaic (PV) technology has evolved rapidly in the past few decades and now encompasses a large variety of materials and device structures. A key aspect to be taken into account in any PV technology is the operational durability under real outdoor conditions, as well as the sustainability of materials/components and the facile integration with energy storage systems.

In the last five years, dye-sensitized solar cells (DSSCs) with water-based electrolytes are considered as one of the possible breakthroughs towards DSSCs large-scale diffusion. If opportunely developed and optimized, aqueous solar cells can be truly considered a zero-impact photovoltaic device with no toxic components (1, 2). Moreover, the possibility of gellyfing the electrolyte into a solid matrix can reduce the leakage outside the device, thus increasing the long-term stability (3). In this respect, we present bio-derived polymers as promising candidates for electrolyte stabilization, being renewable and easy available at low cost.

At the same time, the increasing energy request in off-grid conditions is forcing the scientific and industrial community to explore the feasibility of integrated PV-based harvesting storage devices. To this purpose, DSSCs and electrical double layer capacitors (EDLCs) combinations are reaching wide attention, also thanks to the simple configuration, long cycle life and high power density of the latter. Here we present different platforms applied for the fabrication of innovative self-powered devices integrating energy harvesting and storage sections (4, 5).

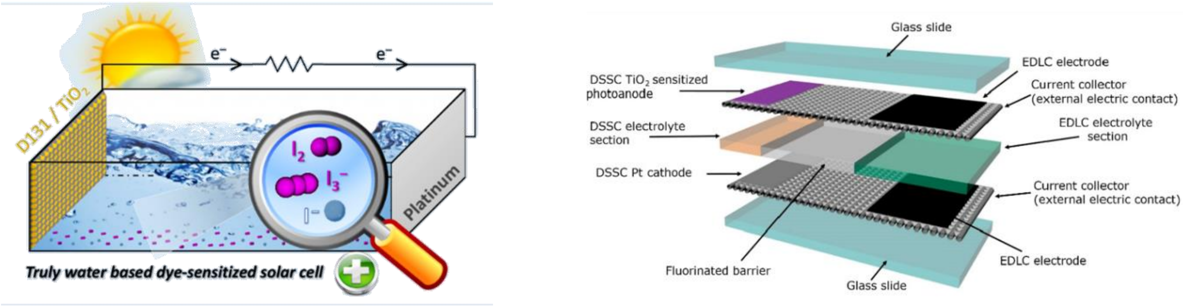

Figure 1. (left) Scheme of an aqueous DSSC; (right) Scheme of an integrated DSSC/EDLC device.

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WS4 PO03

Rates of Elementary Charge Separation and Charge Recombination Processes in BHJ solar cells

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The rates of the elementary charge separation, charge recombination, and charge diffusion processes occurring in bulk heterojunction solar cells have been evaluated from first principles, employing the Fermi Golden Rule and Kubo's generating function method for evaluating the Franck−Condon weighted densities of states (1), with equilibrium geometries, vibrational frequencies, normal modes, and electronic coupling terms computed at density functional theory level.

p-DTS(FBTTh$_2$)$_2$, see figure 1, and PC$_{70}$BM has been considered as electron donor and electron acceptor species, which in bulk heterojunction solar cells yielded a significant high power conversion energy, of about 7 % (2). Both singlet and triplet low lying energy states have been considered, in order to account for the possible formation of triplet excitons from nongeminate charge recombination processes. The results show that the higher performance of p-DTS(FBTTh$_2$)$_2$ with respect to other dyes previously analyzed (3) is due to the presence in its crystalline form of two paths with high electronic coupling leading to efficient hole diffusion inside donor domains.

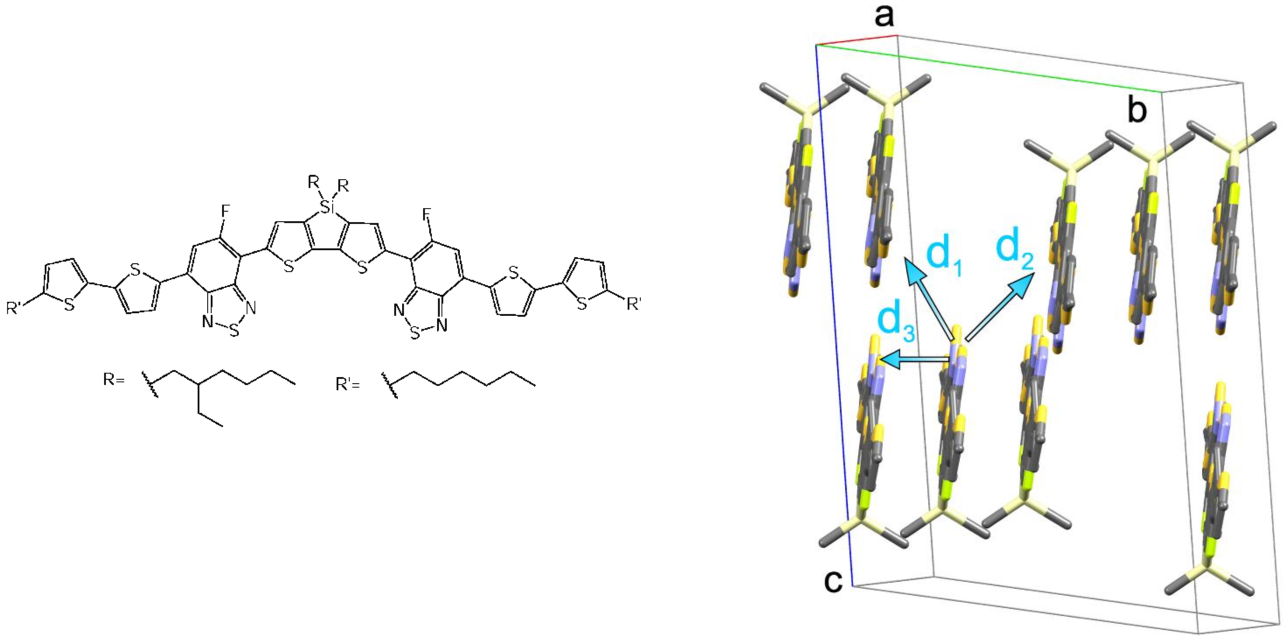

Figure 1 Chemical structure of p-DTS(FBTTh$_2$)$_2$ and its solid state arrangement, with the main hole diffusion path.

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WS4 PO04

Designed long-lived luminescence in quantum dot-chromophore conjugates

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Reversible electronic energy transfer (REET) has been investigated in a range of molecule-based bichromophoric systems, including molecular dyads (1,2) and non-covalent assemblies (3,4). Herein we report evidence of REET involving colloidal luminescent semiconductor Quantum Dots (QDs) endowed with appropriate chromophoric units bound to their surface (Figure 1). In our system, the emitting level of a proper CdSe QD sample undergoes an equilibration with the energy-matched triplet excited state of 1-pyrenecarboxylic acid (1-PCA), which ultimately results in the elongation of the lifetime of the QD by several orders of magnitude. Solid experimental evidence supporting the occurrence of such a process was observed, and QDs exhibiting the typical Gaussian-shaped emission band and luminescence lifetime up to 200 µs were obtained. Moreover, the effect of the oxygen and of the size of the QDs was also investigated (5).

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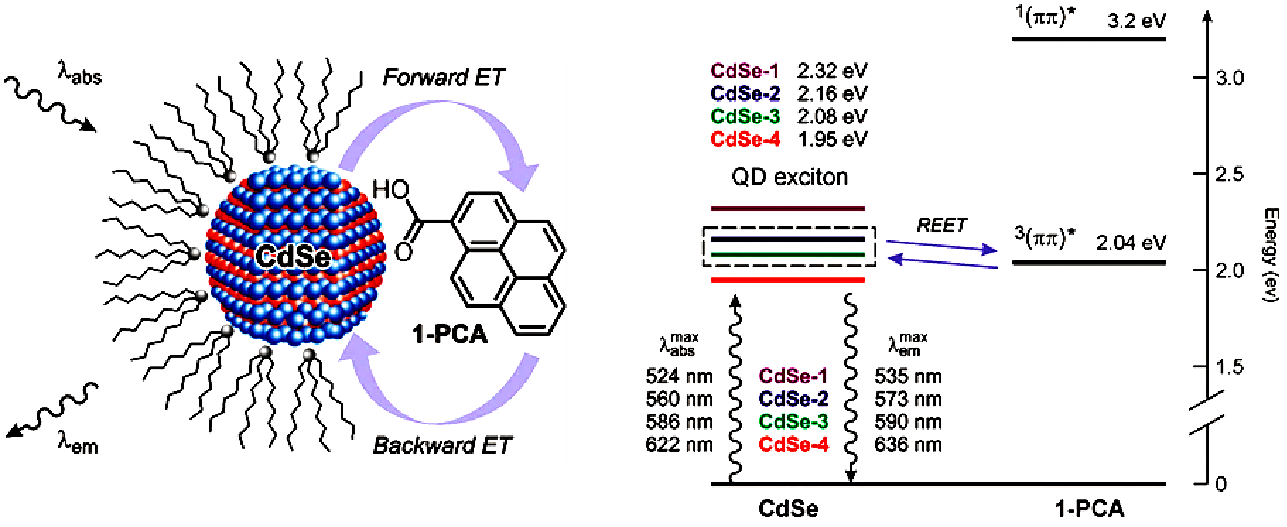

Figure 1. Energy-level diagram of CdSe QDs decorated with 1-PCA. The excitonic level of only CdSe-2 and CdSe-3 are energy-matched with the lowest triplet state of 1-PCA for the REET process to occur.

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WS4 PO05

Development of novel deposition strategies of nano-TiO_2 onto unconventional substrates for wastewater treatment

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The exponential increase of human activities causes harmful consequences for the environment. In this context, water resources are gaining increasing attentions due to the occurrence of emerging pollutants including dyes, pharmaceutical and personal care products (PPCP), endocrine disruptors, pathogens; for this type of pollutants traditional methods show limited performances.(1) The interest of the scientific community has been focusing on alternative methods as the Advanced Oxidation Processes (AOPs).(2) Among AOPs, TiO_2-based photocatalysis has recently emerged as a promising water treatment. In particular, nanosized TiO_2 demonstrated improved performances with respect to its bulk counterpart, thanks to its extremely high surface-to-volume ratio which can greatly increases the density of active sites available for adsorption and catalysis. In addition, the size-dependent band gap of nanosized semiconductors allows tuning the red-ox potentials to achieve selective photochemical reactions. The new frontier for the use of nanostructured photocatalysts is their immobilization onto solid surfaces.(3) In the present work, we studied two type of deposition techniques, namely doctor blade method and a purposely developed dip coating procedure (here referred to as "inverted dip coating"), to coat TiO_2 NPs first on glass substrates, and successively the more performing method was used to coat on unconventional substrates stainless steel mesh. To this end, a batch of TiO_2 NPs was synthesized by suitably modifying a reported approach, specifically selected for its scalability.(4) UV-Vis absorption spectroscopy, X-ray diffraction analysis and TEM microscopy were used to characterized the obtained product. TiO_2NPs-based coatings were obtained by means of the *doctor blade* technique and the *inverted dip coating* method, from isopropanol suspensions of TiO_2 NPs, at a concentration of 6,5%, 13% and 26% by weight, respectively. The morphology of the resulting coatings was investigated by SEM analysis and allowed to detect significant differences between the coatings fabricated by using the two deposition techniques. The difference between the substrates produced by the two techniques is linked to the homogeneity of the film: with *doctor blade* method appear inhomogeneous with presence of superficial cracks. On the contrary, more homogeneous coatings, without cracks were obtained by using the *inverted dip coating* method. The photocatalytic activity of the prepared coating was assessed by monitoring the decolouration of a model target molecule, Methylene Blue (MB), in aqueous solution under UV light irradiation. The inverted dip coating is the most versatile deposition method for real applications. The TiO_2 NPs were then deposited on stainless steel mesh by using isopropanol suspensions at 6,5% and 13%. TiO_2 NPs content. Also, the films deposited onto the stainless steel meshes were thoroughly investigated by SEM microscopy and by measuring their photoactivity. The experimental results revealed that, considering both the photocatalytic performance and the quality of the films, the coatings obtained by inverted dip coating method at 13% TiO_2 NPs contents onto stainless steel mesh result to be the most promising for real applications.

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WS4 PO06

Design of colloidal QD dimers towards quantum optical coherence

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The semiconductor devices industry is constantly challenged to achieve a better control at the nanoscale. Efforts to miniaturize electronic devices point in various directions, including the exploitation of new materials and the use of self-assembly (1) that enables a control on the construction of solid structures at the atomic scale. At such a scale, quantum phenomena begin to dominate, resulting in change of the device behaviour. For example, in closely connected semiconductor nanocrystals systems, quantum coupling must be taken into account.(2) Among the advanced materials that can be used for the implementation of optoelectronic, photonic and sensing application, colloidal semiconductor quantum dots (QDs) are promising materials for realizing nanoscale devices.(3) Most of such device implementations use a large number of aggregated QDs, with not well defined interparticle distance. Only few studies in literature concern the fabrication and characterization of nanostructures composed of a low number of QDs. In addition, the colloidal approach allows to play with the surface chemistry of QDs and tune the interparticle distances. The investigation of the properties of such QD based molecules allow a better understanding of the mechanisms underlying the coupling of QDs. Functionalization strategies based on ligand exchange procedure have been performed to tune the quantum dots (QDs) surface chemistry promoting the approaching of QDs to each other to form a dimer. Bifunctional ligands have been explored as potential molecular bridges that can promote the control of nanocrystal assembling into dimeric and multiple nanostructures, having a fine control on the interparticle distance at nanometric and sub-nanometric range. The capping agents have been properly selected to modulate the interdistance between the nano-objects and to promote transfer processes in the coupled dimeric system. The results allow inferring that the exciton dissociation can be induced by inter-dot coupling, via tunnelling, opening the way to possible coherent phenomena between neighbouring QDs.

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WS4 PO07

Water-processable blend nanoparticles for sustainable organic solar cells

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Organic photovoltaic (OPV) technology has been intensively investigated over the last decades as it represents an intriguing alternative for electrical power generation. Nevertheless, its market penetration is limited not so much by the lower power conversion efficiencies, but rather by the use of halogenated organic solvents, which are toxic and harmful (1,2).

Polymer-based water-processable nanoparticles (WPNPs) represent a way to overcome the problem. They received considerable attention in the OPV field because their morphology can be modulated in order to optimize the interpenetrating electron donor/acceptor networks and thus to improve the device performance (3,4). Usually, WPNP dispersions are obtained through miniemulsion method using huge amount of surfactants. This approach makes it possible to reduce hazardous solvents in the active layer fabrication, increasing the sustainability of the process. However, surfactants display an insulating behaviour and have to be removed (5).

Recently our research group developed the preparation of polymer-based WPNPs dispersions through miniemulsion approach using amphiphilic rod-coil block copolymers (ABCPs), bearing a rigid block (a p-type semiconducting polymer) and a hydrophilic flexible segment. Amphiphilic rod-coil block copolymers are able to self-assemble, generating organized nanostructures under specific conditions (6). The hydrophilic flexible block works as surfactant, interacting with aqueous medium and thus assuring the colloidal suspension stability (7). In addition, it interacts with the electron acceptor material (n-type), leading to the formation of pre-aggregated domains, whose dimensions are comparable with the exciton diffusion length. ABCP series, PCPDTBT-*b*-P4VP, were synthetized constituted by a low band gap copolymer (LBG), PCPDTBT as rod, and tailored segments of poly-4-vinylpyridine (P4VP) as hydrophilic flexible coil. Furthermore, their ability to form WPNP dispersion in aqueous medium through miniemulsion approach, neat or in blend with fullerene derivatives, was investigated. The so-obtained WPNPs were optically, morphologically and electrically characterized, and were tested as active layer in sustainable polymeric solar cells (8).

We are developing new series of LBG-based WPNP dispersions in order to enhance the solar radiation absorption. Materials characterized by a higher degree of crystallinity have been selected to investigate the nanoscale structural organization of the p-type material inside the so-obtained WPNPs.

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WS4 PO08

Block copolymer based hybrid nanocomposite materials for photovoltaic applications

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Nanoscience is still searching for simple methods to arrange nanosized objects by means of bottom-up processes. Composite structures on the nanometer length scale are very promising candidates for next-generation materials (1). Very important in this framework is the incorporation of nonpolymeric properties into polymeric matrices. It is well known that metal nanoparticles (NPs) possess unique, size-dependent properties associated with their extremely large specific surface area. Those properties can be exploited through the immobilization and the assembly of nanoparticles on an appropriate substrate. Self-assembly processes are the method of choice to achieve this goal.

Microphase separation of block copolymers (BCPs) is a well-studied phenomenon able to spontaneously produce ordered nanostructured morphologies (spheres, cylinders o lamellae) depending on the relative lengths of the polymer blocks (2). Most importantly, BCPs domains sizes can be controlled from a few to several tens of nanometers, and in turn can act as hosts for sequestering nanoparticles of appropriate chemical affinity and geometry (3).

Surface decoration of NPs is a procedure often used to stabilize them against aggregation and to assure the selective inclusion in one of the BCP domains by chemical compatibility. In this way the NPs will reflect the regular organization of the BCP domain in which they are embedded. Considering the precise control over the domains dimension and organization that BCPs can achieve by self-assembly, the nanocomposite materials fabricated using BCPs as host for sequestering functional NPs according to precise morphologies represent very promising engineering nanostructured materials endowed with unprecedented properties.

In the present work a symmetric diblock copolymer, polystyrene-block-poly(methyl methacrylate) (PS-*b*-PMMA), able to give by self-assembly a lamellar morphology, was used as host for the selective inclusion of *n*- and *p-type* semiconductor NPs in different nanodomains, with the aim of using them as photoactive layers in bulk heterojunction solar cells devices. The inclusion of the two NPs in the BCP lamellae will create a bi-continuous interpenetrate network of charge carriers between the two electrodes, minimizing charge recombination and thus increasing the device efficiency. Morphologies characterized by the desired degree of order and orientation of nanodomains were obtained resorting to indium tin oxide (ITO) as transparent support, a grafting to approach, consisting in covering the ITO surface with a styrene-methyl methacrylate random copolymer (RACO) (4), deposition of PS-*b*-PMMA on the so neutralized ITO surface, coupled to appropriate thermal annealing procedures of the final ITO/RACO/BCP systems. In the successive step, a procedure was set up for the selective removal of PMMA blocks by means of far-UV radiation treatments, with the purpose of generating channels characterized by a width of the order of a few tens of nanometer onto ITO surface. Metal NPs, ZnO and CdSe, were synthetized with appropriate surface functionalization in order to assure their selective inclusion in the PS and the nanochannel left free upon PMMA blocks removal, respectively. The BCP morphology and the NPs inclusion were assessed by a transmission electron (TEM) and atomic force (AFM) microscopy analysis.

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WS4 PO09

Nanostructured photocatalysts combined with UV radiation for water treatment

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Scarcity of fresh water has escalated to be one of the major global problem as goal 6 of Agenda 2030 “Clean water and sanitation” witnesses. Actually, traditional wastewater treatment technologies have several drawbacks such as high-energy requirement, generation of toxic sludge and are not adequate to provide safe water due to increasing emerging contaminants that are persistent to the conventional methods. Therefore, it exists an urgent demand for new methods to improve the efficacy of wastewater treatment (1).

Removal of emerging contaminants can be performed by applying separately or in combination advanced abiotic treatments such as membrane filtration, UV degradation, ozonation and advanced oxidation processes (AOPs) (2). An AOP typically involves the formation of hydroxyl radicals (•OH), among the strongest oxidizing species commonly used for water treatment carrying out the oxidation and degradation of target species. UV-based AOPs involve the addition of an oxidant or photocatalyst that UV photolyzes or activates leading to the formation of •OH radicals (3, 4). Wide band gap semiconductors are used as photocatalysts in AOP as the redox potential of •OH/H_2O pair falls in their band gap, thus photogenerated electron-hole (e-/h+) pairs can react with dissolved oxygen or water, respectively, to generate •OH (5, 6). Common limitations in the use of the different semiconductors (e.g. ZnO, Fe_2O_3, CdS, etc.) are visible light transparency, colloidal instability and fouling, catalyst recovery, low activity, etc. Among the different semiconductors, TiO_2 still receives the greatest attention being an efficient/low cost, and chemically and biologically inert photocatalyst. Nanomaterials, thanks to their unique properties (e.g. high surface-to-volume ratio leading to a high density of active sites for adsorption and catalysis), are showing a good potential to be exploited as photocatalysts within AOP for emerging contaminants removal in combination with UV radiation.

FONTANAPULIA and TARANTO are public funded projects managed by a public-private partnership aimed at developing the combination of different AOPs treatments - UV treatment assisted by nanostructured photocatalysts - for the abatement of emerging contaminants. To increase the photocatalytic activity, design, lab and up-scale synthesis of wide band gap nanomaterials such as nanostructured TiO_2 are under investigation. Moreover, the application of nanostructured photocatalysts in real cases is strongly hampered by the difficulty of recovery of the nanosized photocatalysts, that would compromise the quality of the effluent. In order to overcome such a limitation, the design and implementation of an efficient nanocatalysts deposition technique is under development. The evaluation of the technology at the pilot scale, is planned to be performed by carrying out the final test in an industrial wastewater treatment plant.

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WS4 PO10

Luminescent Solar Concentrators based on Silicon Nanocrystals

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Proposed by Lerner et al.[1] in the 1973, luminescent solar concentrators (LSCs) represent nowadays one of the possible solutions for a sustainable future.[2] LSCs are systems, typically in the form of plates, which convert sun light into electricity by exploitation of the optical phenomenon called total internal reflection (TIR). Luminescent chromophores are embedded inside a transparent waveguide (glass or polymeric one) or deposited above it. Upon solar light excitation the luminescent species emit light that is directed to the edges of the system by TIR, where a photovoltaic cell is placed. This architecture allows the conversion of a certain amount of light into electricity; the remaining part of the solar spectrum passes through the coloured or semi-transparent matrix, opening the way to the building of photovoltaic windows: "Solar Windows".

In this case, silicon nanocrystals (SiNCs)[3] in the quantum size range (diameter=2-12 nm) have been used as a luminescent species, able to absorb in the near UV and emit in the NIR, remaining transparent in the visible spectral region. Compared to more traditional quantum dots, such as CdSe, SiNCs offer several advantages such as the lack of toxicity, the abundance of the main component, the high sustainability and the high Stokes-shift due to the indirect band gap nature.

In this study, solution phase, SiNCs were functionalized with 1- dodecene through a low temperature approach and they were i) embedded in acrylic polymer matrix by thermally initiated bulk co-polymerization, ii) dissolved in a polymeric solution and deposited on a transparent substrate in order to obtain a thin film.

Once the LSC was obtained it was possible to characterize its morphology, its optical and structural properties.

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WS4 PO11

Design of 3D printed chitosan-TiO_2 scaffolds for removal of amoxicillin from wastewater by photodegradation

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TiO_2-supported chitosan scaffolds (TiO_2/CS) are here proposed as promising material for wastewater treatment, in particular for the removal of amoxicillin by photodegradation under UV/Vis irradiation. Due to the release of antibiotics in wastewater and their persistence in the environment, harmful effects can develop on the aquatic and terrestrial organisms. TiO_2 chitosan scaffolds with photocatalytic activity have been prepared by 3D printing using commercial TiO_2. The formulation for the 3D printer was prepared by dispersion of chitosan and TiO_2 in powder (1). The TiO_2 particles embedded in the chitosan are homogeneously distributed in the scaffold also after repeated photocatalytic tests, as revealed by SEM-EDS.

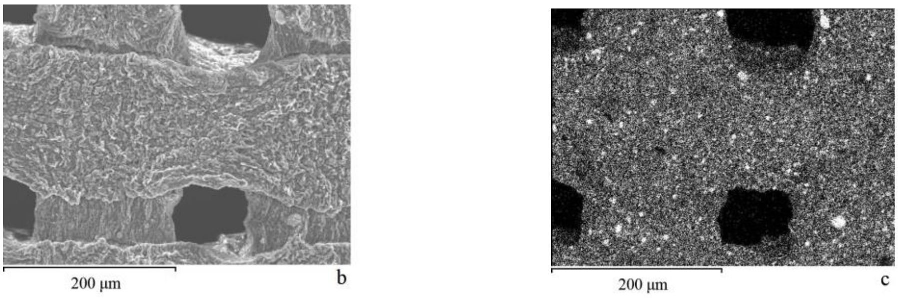

Fig. 1. SEM image of TiO_2/CS after the photocatalytic tests (left); EDS Ti map (right)

The advantage of 3D printed scaffolds embedding TiO_2 is represented by the possibility of modulating their shape and size, thus offering a very high area/volume ratio, crucial parameter for amoxicillin photocatalysis. Three dimensional scaffolds can serve as fixing substrates for TiO_2, since their mechanical properties are suitable for handling, manipulation in the industrial environments and they might constitute a prototype of filters for cleaning water discharges. Degradation kinetics of AMX achieved using TiO_2/CS scaffolds is almost as fast as that obtained with pure TiO_2 powder, making them innovative tools, easy to produce in series and reusable for water purification from pollutants such as amoxicillin, having a positive impact on the environment rather than for drinking-water.

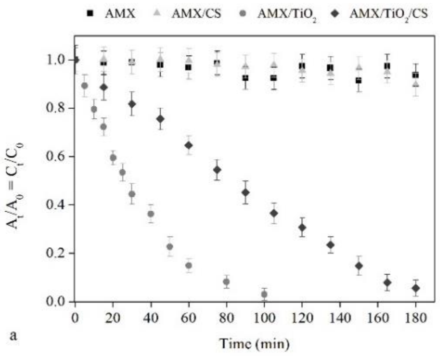

Fig. 2. Photolysis and photocatalysis of AMX versus time.
[Degradation monitored by UV_{230} measurements].

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WS4 PO12

Noble metal-free photocatalytic hydrogen evolution on gel-derived defective TiO_2

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Titanium dioxide is one of the most attractive semiconducting oxides. The need to enhance specific functional properties of the material, e.g. to extend the photoresponsivity to visible light and to increase the photocatalytic efficiency, leads to different strategies for the modification of its electronic structure (1, 2). Hydrogen production from water is the most intensely sought energy application of photocatalysis. The present work is addressed to synthesize stable TiO_{2-x} materials with a controlled population of defects, starting from hybrid chemical gels in which titanium is involved in a charge transfer complexation equilibrium with an organic compound (3). Both the sol-gel procedure and the following thermal treatments of the gel in mild conditions have synergistic effects in determining the characteristics of the final product. We report the synthesis of bulk TiO_2 materials featuring a defective structure without evidence of the presence of Ti^{3+}, as substantiated by X-ray photoelectron spectroscopy. The electronic properties of the samples were investigated also by EPR and THz spectroscopy. We found that graphitic carbon derived from the organic component has a primary influence on the properties and photocatalytic activity of these samples, tested in hydrogen generation using glycerol as electron donor (photoreforming). They showed significant yields of H_2, especially under UV irradiation, but also under visible light.

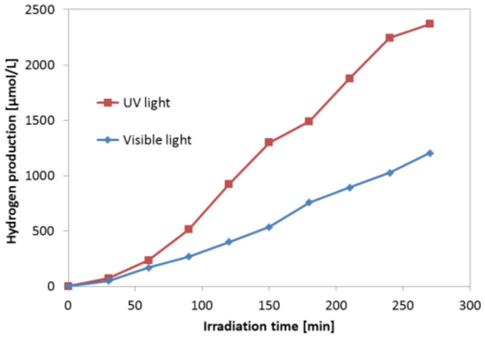

Figure: Photocatalytic H_2 production from glycerol aqueous solution during the irradiation time.

In particular, after 270 min of irradiation, the H_2 production was about 2400 and 1200 µmol/L under UV and visible light, respectively. These results are really encouraging considering the absence of noble metal co-catalysts in the synthesis of the material. Furthermore, the stability of the photocatalytic activity was evaluated. The photocatalyst proved to be effective even after 5 cycles of use, keeping the H_2 production almost unchanged after 4 h of UV irradiation.

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WS4 PO13

Pre-slaughter feed restriction beneficially influences gastric digestibility of sea bream (*Sparus aurata L.*) fillet

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Gilthead sea bream (*Sparus aurata L.*) is intensively raised in fish aquaculture production, which is focused on optimizing the feeding regime for best performance and sustainability. This species, as well as many other species of fish, exhibit remarkable resistance to starvation compared to mammals. However, following prolonged food deprivation muscle protein tissues start to be intensively degraded (1). The aim of this study was to investigate if sea bream raised under aquaculture conditions can adapt to a starvation regime of 21 days by assessing the effects of this regime in comparison to a full ration control on the main myofibrillar protein degradation. In addition, human gastric digestibility of fillets was evaluated under conditions relevant to the treatment of the gastroesophageal reflux disease (GERD). Protein identification by mass spectrometry (MS/MS) was performed after Western blotting (WB) on protein separated by SDS-PAGE. In the early post-mortem, actin fragments were detected in both the samples regardless of the feeding regime, while only in the starved fish samples myosin light chain was found markedly degraded, consistent with its natural instability in comparison to the mammal protein. By using a static standardized in-vitro digestion method (2) actin was found susceptible to full proteolysis, irrespective of the feeding regime and the experimental variation of pH, whereas digestibility of myosin was found to increase in the starved samples when individual test enzymes were applied under conditions of drug-induced high pH occurring in GERD patients. Therefore, it appeared that under conditions that caused an early degradation of the myosin light chain and possibly an impaired myosin integrity, digestibility of the protein was much higher. In conclusion, sea bream feed restriction, other than decreases the environmental impact of fish aquaculture, seems to act on the already unstable nature of the fish myosin, resulting in nutritional benefits for the increasing number of people under acid-suppressant therapy for GERD.

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WS4 PO14

Luminescent boron-functionalized benzodithiophenes

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Tricoordinate boron-functionalized molecules, such as triarylboranes, have recently emerged as a powerful new class of electron acceptors with great potential for application in optoelectronic n-type materials (1, 2). This electron-accepting ability is the result of the p–π* conjugation between the empty p orbital of boron atom and the π* orbital of the π-conjugated framework. Furthermore, aromatic organo-boron systems often show fluorescence emission in the visible range of the electromagnetic spectrum and capability to detect strong *Lewis* bases (CN^-, F^-). In recent years many examples of boron-functionalized molecules have been reported but, given their unique n-type semiconducting features, the design of new structures is still an attractive and relevant research topic. We present the synthesis of new triarylboranes **1**–**4** containing linear or angular benzodithiophene (BDT) as core molecule and bearing one or two dimesityl boryl groups (Figure).

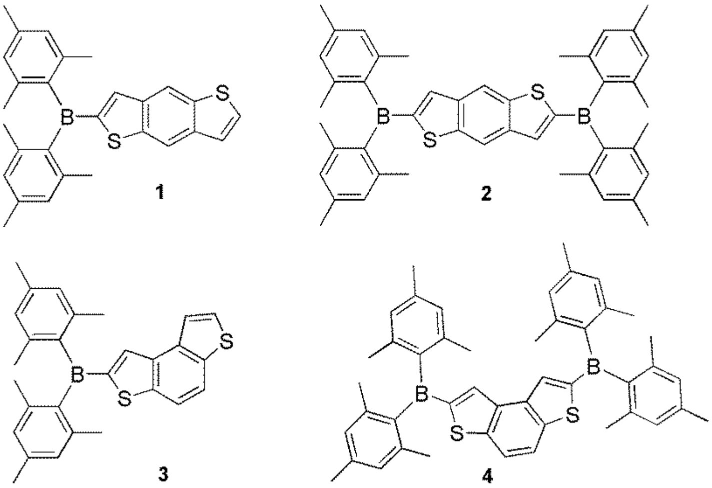

Figure. New BDT-based triarylboranes.

Photophysical and electrochemical studies were carried out to evaluate the potential of structures **1**–**4** as building blocks of materials for optoelectronic applications. In particular, compound **2** was selected as the most promising candidate since it shows good luminescence performances ($\lambda_{max} = 470$ nm; $\Phi = 0.57$), redox properties and capability to detect fluoride anions.

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WS4 PO15

Photocatalysts in the formulation of traditional Venician *Marmorino*

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The project aims to develop innovative materials and technologies for Restoration and Cultural Heritage, focused in particular for traditional Venetian buildings[1]. The idea was to design high-performance multi-functional nanostructured materials that can degrade the main environmental pollutants (NOx, VOC) by photocatalysis, reduce bacterial attacks and give self-cleaning properties[2]. The materials were used in the formulation of the Venetian *marmorino* in collaboration with the Union of Venetian Plasterers (Uni.S.Ve. Srl).

Marmorino is a typical wall covering of the Venetian tradition, used both inside and outside the buildings. What distinguishes it from a common plaster is the presence of marble dust inside the composition of the dough, and the technique of spreading *in fresco*. The photocatalysts were applied both inside the *marmorino* and as a surface coating, "as it is" and combined with two of the traditional coating techniques of natural Venetian *marmorino* (lime and soap).

Two photocatalysts based on titanium dioxide (one commercial and one lab-made) and two based on zinc oxide (a commercial and one lab-made) were investigated. Methylene blue was used to simulate surface degradation, as model organic pollutant, and evaluate the photocatalytic properties of materials by colorimetric analyses. Several characterization techniques (XRD, N_2 physisorption, SEM and EDX) were used for both pure oxides and their formulations with *marmorino*.

First, the photocatalytic materials were applied inside the mixture (20 wt%), but the results were not optimal. In fact, it was assumed that the photocatalysts, although applied in the most superficial layer of the *marmorino*, were not able to receive enough light radiation to be activated. At the same time, they suffer of mass transport limitation of oxygen in the deep layers of the materials. Only the sample based on lab-made ZnO was able to degrade 73% of dye after 4 hours under visible light. The photocatalysts were then used as surface coatings, applied "as it is" and combined with two of the traditional coating techniques of natural Venetian *marmorino* (lime and soap). In this case, the formulates performed very well. Best results were obtained with commercial TiO_2 and lab-made ZnO samples with the soap coating technique. This is reasonably due to the proper size of oxide crystallites and of surface area for these two photocatalysts. These doped *marmorini* degraded 95% and 82% of the applied dye respectively, while the not doped material degraded only 6%. In both samples, we hypothesize the presence of a synergistic effect between the metal ions of Fe and Cu, present in the soap, and the photocatalysts. In fact, without soap the degradations were 70 and 20% respectively for commercial TiO_2 and lab-made ZnO photocatalysts used as surface coating.

Moreover, the coating obtained with ZnO retained also high transparency, a quality that plays an important role in an application for Cultural Heritage.

Through this work it was therefore demonstrated that it is possible to combine the Venetian tradition with the innovation of research on nanostructured materials, obtaining products for the restoration and conservation of cultural assets, which are both innovative and multifunctional, with green characteristics that do not distort traditional natural products.

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WS4 PO16

Development of high capacity lithium sulphur batteries

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Livia Della Seta[a]

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In a rapidly changing electrical system scenario, where the energy mix sees an increasingly massive penetration of energy from renewable sources, technological solutions for the accumulation of electrical energy will progressively acquire a fundamental role. Recently, innovative storage systems have been developed, in particular lithium-ion batteries, with a double or triple energy density compared to other previous technologies (1,2). Nevertheless, further technological progress and greater cost competitiveness are required for the development of storage systems for electro-mobility or stationary energy storage. To increase the energy density of the energy storage systems, it is necessary to use innovative electrochemical materials and systems. Lithium sulfur batteries (Li-S) are promising candidates to replace lithium ion batteries because they are cheaper, lighter and, for the same weight, can store almost twice as much energy (3,4). In this presentation we want to show some of the most recent results obtained in our laboratory concerning the fabrication of lithium sulphur batteries (5). For their construction we used two different binders and two carbons with different surface area, deposited directly on the separator. Sulphur was introduced mixed with the electrolyte in the form of polysulphide. The particular cell configuration has allowed to obtain stable specific capacities after numerous charge and discharge cycles of more than 800 and 1200 mAh g^{-1} and low cell resistances.

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WS4 PO17

New materials for luminescent solar concentrators

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The concept of Net Zero-Energy Buildings (NZEBs) is receiving an increasing amount of attention by the scientific community and policy organizations, such as the European Committee (1). NZEBs are technically feasible for individual houses and small buildings due to rooftop photovoltaic (PV) cells and efficient insulation. Nevertheless, being ~7 m^2/kW the peak power needed for NZEBs, the use of PVs is not worthwhile for larger buildings (2). An accessible solution to this problem is represented by luminescent solar concentrators (LSCs). LSCs are optical devices that absorb sunlight, re-emit the light via fluorescence that is concentrated at their sides, where it can be converted into electricity by photovoltaic (PV) cells. LSCs are semi-transparent so that they leave the aesthetics of buildings mostly intact. To date, Current state of the art host polymers are commercially available polymethylmethacrylates (PMMA) that also show good compatibility with a wide variety of high quantum yield fluorophores (3). Nevertheless, the oil-based nature of this polymer is a critical drawback for modern urban areas, being the use of solar harvesting systems or devices based on renewable materials and eco-friendly deposition methods also highly desirable. This study reports examples aimed at favoring the diffusion of the LSC/PV technology in urban area, and based on the utilization of new host bio-based matrices (4) and alternative deposition methods on glass surfaces. Different organic fluorophores were utilized depending on their optical characteristics and solubility in the selected polymers. The results and the devices performances were discussed also in terms of the most recent literature on this topic.

Acknowledgements
This work was supported by the Bando Dimostratori Tecnologici of the University of Pisa

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WS4 PO18

Environmental Applications and Organic Syntheses in a UVA-LEDs Photocatalytic Fluidized Bed Reactor

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Photocatalysis is an “green” technology with potential applications in various disciplines, such as chemical synthesis and environmental technology. For the industrial application, photocatalytic reactors design mainly requires to overcome actual mass and photons transfer limitations. Fluidized bed reactors are well known in enhancing mass transfer. With respect to photon transfer, microscale illumination systems by LEDs seem to be a promising solution (1). We have developed a gas-solid photocatalytic fluidized bed reactor at high performances (2). The device couples positive aspects such as wide exposition of catalyst to the radiation to the effective use of UVA LEDs which are long-lasting, robust, small in size and high in efficiency. In this work different photocatalytic applications in the high efficiency gas-solid photocatalytic reactor are reported.

MoO_x/TiO_2 and VO_x/TiO_2 catalysts were prepared by wet impregnation of anatase titania sample with an aqueous solution of ammonium heptamolybdate or ammonium metavanadate respectively, followed by calcination in air at 400°C. Sulphated $MoO_3/\gamma\text{-}Al_2O_3$ photocatalysts were prepared following the method reported in (3)

Photocatalytic tests started feeding the reaction gaseous mixture to the photoreactor at reaction temperature in dark. After the complete adsorption of hydrocarbon on the catalyst, UVA-LEDs were switched on. In the absence of light, no reaction products were observed. This system allows to realize the photocatalytic deep oxidation of volatile organic compounds such as toluene, benzene and acetone on V_2O_5/TiO_2 catalysts, with a contact time of 300 ms in a small reaction volume (0.1L). By selection and optimization of catalyst formulation, selective photocatalytic oxidation of hydrocarbons can be achieved, see Table 1.

Table 1

Reaction	**Catalyst**	**Hydrocarbon conversion %**	**Selectivity %**	**Reaction temperature,°C**
Benzene to CO_2	V_2O_5/TiO_2	27	100	80
Cyclohexane to benzene	MoO_3/TiO_2	33	99	120
Cyclohexane to cyclohexene	$MoO_3/\gamma\text{-}Al_2O_3$	28	100	120
Ethylbenzene to styrene	$MoO_3/\gamma\text{-}Al_2O_3$	27	100	120
Ethanol to acetaldehyde	V_2O_5/TiO_2	100	97	100

The UVA-LED photocatalytic fluidized bed reactor was useful both for removing volatile organic compound and for partial oxidation reactions under mild conditions with high selectivity avoiding catalyst deactivation phenomena, resulting of high productivity and adaptability.

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WS4 PO19

Time-saving formulation of Nickel-free 3D graphene for Visible-Light photocatalysis

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One of the most persistent problem affecting the twenty-first century is the environmental pollution and the insufficient access to clean and sanitized water. The visible-light photocatalysis (VLP) represents one of the most promising environmental-friendly technology, taking advantage in the use of solar-light as clean and renewable source. In this context, porphyrin derivatives as organic semiconductors are particularly interesting due to appropriate HOMO and LUMO energy levels and very strong absorption of the Soret band in the 400–450 nm region, as well as the Q-bands in the 500–700 nm region. However, their application is strongly limited by a rapid electron-hole recombination process due to aggregation phenomena. To overcome this, in our recent work, we presented as a proof of concept, the assembly of porphyrin-based polymers via non-covalent π-π* interaction with 3D-Graphene (3DG) grown on Nickel foam template by Chemical Vapor Deposition (CVD) technique. In fact, the combination with graphene represents an efficient method to avoid the electron-hole recombination mechanism, obtaining at the same time a freestanding photocatalytic material with promising photodegradation ability for water treatment (1).
In addition, in this work we proposed the formulation of the freestanding material via a time-saving etching procedure (see Figure 1) to remove Nickel substrate (2). The latter, could constitute a critical issue being released as Ni^{2+} in water during the purification step. Moreover, its removal can determine higher graphene surface exposure to the light irradiation improving the electron transfer process from porphyrin to graphene and thus, the photocatalytic activity. The photoability of the novel Ni-free hybrid composite was evaluated by photodegradation of Methylene Blue. Photoluminescence measurements were performed as well as free-radical and hole scavenging measurements. Finally, we propose a photocatalytic mechanism, reporting for the first time the HOMO and LUMO energy levels of poly-porphyrins calculated by electrochemical study.

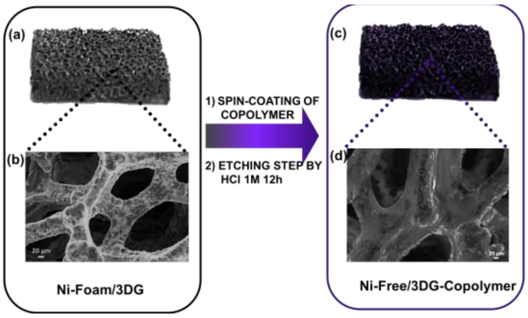

Figure 1. **(a)**, **(b)** an as-grown 3DG coated with a thin layer of cyclic porphyrin copolymer by a spin-coating deposition method and **(c)**, **(d)** a Ni-free/3DG copolymer sample after etching by hot HCl 1M solution maintaining the typical 3D graphene structure.

References: 1. Ussia M. et al, Sci. Rep., Freestanding photocatalytic materials based on 3D graphene and polyporphyrins 2018, 8:5001; 2. Ussia M. et. al, Hybrid Nickel-free graphene/polyporphyrin photocatalyst: time-saving formulation and photodegradation studies (under submission)

WS4 PO20

Population Analysis of Molecular Computational Identification (MCID) of Small Objects and its Extension to the Near Infrared Region

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Molecular logic-based computation (MLBC) (1-3) has grown steadily over the past quarter century (4) with applications in intracellular computation (5, 6) which cannot be mimicked by semiconductor-based devices. However, the first application for MLBC barred to electronic logic devices was molecular computational identification (MCID) (7). Both these situations require the computing device to be biocompatible and small (<µm) while operating wirelessly. MCID still has few examples (8) and would benefit from further validation and extension. Testing of significant populations (9) is a first step of such validation. The objects used in this study are micrometric polymer beads, which carry MCID tags operating with H^+ input and fluorescence output. Particularly, near-infrared fluorescence is employed in order to open up extra bandwidth beyond the blue-green regions used up to now. Azaborondipyrromethenes are employed as the fluorophore in PASS 1, YES and their parallel combinations. The fluorophores on their own are well-behaved PASS 1 logic gates. On the other hand, a YES gate has an additional receptor appendage, which engages in photoinduced electron transfer (10) with the fluorophore. Fluorescence output is switched 'on' when H^+ binds to the receptor. Under microscopic observation, the H^+-induced fluorescence enhancement factors (FE_{H+}) of individual beads are understandably smaller than those seen during spectroscopic examination of bulk samples. Nevertheless, the bead-to-bead variations of the FE_{H+} values are found to cluster into distinct quasi-Gaussian sets for each logic type (Figure 1). MCID is strengthened as a result.

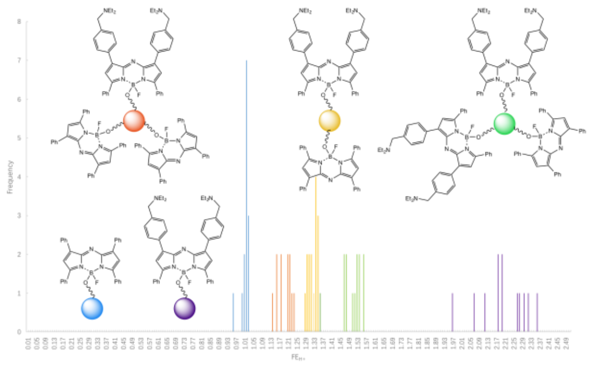

Figure 1. Histogram of the variations of H^+-induced fluorescence enhancements (FE_{H+}) shown by various logic types PASS 1 (blue), 2PASS 1 + YES (orange), PASS 1 + YES (yellow), PASS 1 + 2YES (green), YES (purple).

We thank the China Scholarship Council for support.

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WS5 - SUSTAINABILITY OF PRODUCTS

The workshop aims to foster the interaction between Industries and Research Institutions to address the challenge of sustainability of products. The Industries will present their needs, strategies and results in the field, the Research Institutions their idea, tools and results in a new communication modality that makes more effective to bridge idea to innovation.

Although not limited to only the following topics, the focus of the workshop will be on four main aspects:

- the substitution of SVHC (substance of very high concern),
- the design of new products taking into account the entire life cycle,
- the use of the wastes for the production of new products,
- the design of smart products that are able to decrease the environmental impact of human activity and industrial production.

The main goal of the workshop is to show that chemistry is the solution for the sustainable growth, but that it is necessary to catalyze the mutual interaction between idea and innovation, starting from new, more effective, modalities of communication between Industries, Research and Society.

WS5 - Organizing Committee and Conveners

- Martino Di Serio, University of Naples
- Riccardo Tesser, University of Naples
- Antonio Proto, University of Salerno
- Siglinda Perathoner, ERIC aisbl, Belgium
- Cristiana Gaburri, Federchimica

WS5 - Keynote Lectures

- **WS5 KN01** – Gaetano Iaquaniello, Nextchem Srl, "*Municipal solid wastes valorization through their conversion into syngas*"
- **WS5 KN02** – David Alexander Röttgen, Ambientalex-Law Firm, "*End-of-waste: EU legislation, ECJ-case law and main open issues*"
- **WS5 KN03** – Franco Amelio, Sustainability Leader of Deloitte in Italy, "*Sustainability reporting standards – Deloitte*"
- **WS5 KN04** – Amilcare Collina, Mapei S.p.A, "*Sustainability for MAPEI: facts not words*"
- **WS5 KN05** – Sesto Viticoli, Associazione Italiana per la Ricerca Industriale, "*Responsible Research and Innovation (RRI)*"
- **WS5 KN06** – Nicola Ballarini, Clariant Prodotti, "*The role of sustainability in the manufacture and use of catalysts*"

WS5 KN01

Municipal solid wastes valorization through their conversion into syngas

Gaetano Iaquaniello [a], *Annarita Salladini* [a]

[a] *Nextchem Srl*

Municipal solid wastes, their derived fuels and plastic wastes represent a valid source of carbon to be used in substitution of conventional fossil based feedstock to make chemicals. A proper high temperature gasification step able to convert such wastes into a syngas reach in hydrogen and carbon monoxide is the key to build a new green chemistry paradigm. A production of chemicals such as methanol, ethanol, synthetic natural gas, urea, hydrogen and even polymers is then achievable at a competitive cost of production. The waste-to chemicals represent today a robust alternative to the waste-to-energy route, allowing to fix carbon into useful products instead of downgrading it to CO2. Processes and related economics are here assessed and deeply analyzed, looking also at the process environmental impact. The strategic merger between the waste management and chemical industry is an interesting example of circular economy and represent a fundamental step to create a greater and more sustainable future allowing for better (re)-use of resources and energy.

WS5 KN02

End-of-waste: EU legislation, ECJ-case law and main open issues

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The presentation will highlight, in its first part, the approach held by the EU as well as by single Member States when enacting end-of-waste legislation.

In such context, the analysis will shortly outline the EoW mechanism as provided by directive 2008/98/EC and recently revised by directive 2018/851/EC. The presentation will also provide some examples of who single Member States are dealing, within their national legislation, with EoW.

In its second part, the presentation will focus on recent case law from the European Court of Justice relating to EoW analyzing the most relevant findings.

In its third part, the presentation will briefly highlight the main difficulties and open issues Member States as well as operators are currently facing when approaching and putting into place EoW.

WS5 KN03

Sustainability reporting standards - Deloitte

Franco Amelio[a]

[a] *Sustainability Leader of Deloitte in Italy*

We are experiencing a global environment of changes in the perception of people, present and future strategies of industries, climate change, stakeholders' expectations, compliance requirements, lack of natural resources, complex organizations and value chains. All these factors lead to a need for all stakeholders of more transparent, consistent and reliable information by organizations of all kinds.

This is why reporting standards on sustainability matters are rapidly evolving, aiming to achieve a larger number of practitioners and a higher level of standardization of KPIs among industries and regions: Global Reporting Initiative (GRI) Sustainability Reporting Standards, issued by GRI in 2016. These Standards are used by almost all the Public Interest Entities applying EU Directive on non-financial information from 2017 and by a larger number of companies that are reporting on a voluntary basis.

Learning to use and applying GRI Standards correctly and timely is necessary in order to report information that are comparable among companies and time and are eligible to be assured by third parties (e.g. Audit companies). In fact, sustainability (or non-financial statement) assured by third party is a requirement of local adoption of the EU Directive (e.g. Italy, France, Spain).

Anyway, even with no constrain on assurance, stakeholders (clients, rating agencies, investors, banks, employees, governments, etc.) need to understand and compare information that are becoming more and more of common knowledge. Examples of this are Green House Gases Emissions or gender pay-gap.

Deloitte is acknowledged as a leader in Italy and worldwide in sustainability services ("Deloitte ranked #1 for Sustainability Assurance based on the global sustainability survey by Verdantix") and is appointed by GRI itself as "GRI Certified Training Partner", this enables us to organize training courses on the application of GRI.

Sustainability reporting standards are evolving rapidly, in order to better identify KPIs that represent key performance of organizations, not only for external reporting purposes, but also for internal management reporting (e.g. sustainability targets, MbO on sustainability performances).

It is a continuous improvement and large and cross-function learning environment.

WS5 KN04

Sustainability for MAPEI: facts not words

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The perception of the limits of all the natural resources of the planet, including the environmental resource, heretofore considered unlimited, has led to the widespread sharing of the concept of Sustainability and Sustainable Development.

According to *1987 "Report Word Commission on Environment and Development"* Sustainable development is "development that meets the needs of the present without compromising the ability of future generations to meet their own needs."

The report recalls the three fundamental and inseparable dimensions of development: Environmental, Economic and Social.

Sustainability requires Industry to think more closely about the long-term implications of its activities and to make a responsible use of six forms of capital which are the essential ingredients of all the economic activities of the Company: Natural capital, Human capital, Intellectual capital, Manufactured capital, Social capital, Financial capital.

MAPEI is well aware that the role of a Company in our Civil Society is far greater than that of generating profits and firmly believes that Company's reputation and credit include its ethical and scientific profile, its human and cultural background and its social commitment.

For this reason, MAPEI is adding to the traditional three pillars of its strategy - Internationalization, Research and Development and Specialization – the fourth pillar of Sustainability.

In order to testify its commitment to Sustainability MAPEI decided, since 2016, to draw up a "Sustainability Report".

The last issue is outlining the Mapei Group consolidated Italian activities in 2018 which include, besides Mapei S.p.A., the Companies Adesital, Cercol, Mosaico+, Polyglass, Vaga and Vinavil.

The presentation will highlight the MAPEI approach to economic, environmental and social sustainability as well as the related key figures in 2018 Report.

WS5 KN05

Responsible Research and Innovation (RRI)

Sesto Viticoli[a]

[a] *Associazione Italiana per la Ricerca Industriale*

Considering the technological developments and disruptive scenarios that will be induced by the Fourth Industrial Revolution, it is increasingly important to ensure these changes will be aligned with and help to address the grand challenges faced by society. The whole systems and communities around Research and Innovation should increase their awareness about societal needs and perspectives, and as well about the potential societal impacts related to these new technologies (and of the responsibilities thereof).

A value chain approach should be implemented, facilitating the interconnection of the two systems of Research and Innovation, and allowing them to work toward a common vision of responsibility and sustainability in the experimental development of scientific knowledge.

Applying the principles of Responsible Research and Innovation (RRI) to the Research System – intended as the actors and infrastructures working to develop new knowledge– means proposing an approach to science and research policies based on societal needs, and on the involvement of societal actors, through the implementation of inclusive and participatory approaches in all phases of the research processes. In this context, Open Science (OS) represents a new approach, based on the cooperative work of all major R&D actors (researchers, citizens, businesses, academic and research institutions, funders and policy makers, etc.) and a new path for sharing and accessing knowledge, through the widespread use of digital technologies and collaborative tools. It emphasizes the primary need to share and make accessible (in an open, comprehensible and transparent way) methodologies, knowledge, processes and tools, from the earliest stages of the process of scientific discovery. This is in the first place a cultural change, and thus implies introduction of RRI aspects in the Education system. It also requires developing new models for the Evaluation of Research, going beyond traditional bibliometric analysis, and finding ways to take into account also Science / Society relationships.

When looking at the Innovation system, and thus the business side, the importance of approaches that can help to consider societal aspects is shown by more than two decades of experiences in the fields of Corporate Social Responsibility and Sustainability (economic, social, environmental): lower costs, higher revenues, attraction of investors, risk reduction, anticipation of regulatory barriers, increase of reputation, business resilience, etc. An RRI approach, requires for the business community changes at strategic level, ensuring a culture of Responsibility is endorsed by the executive management, and embedded in the company strategy and the various functions connected to research and innovation. RRI implementation need as well to be adapted to the realities and constraints of the companies and specific sectors considered, including the differences in terms of type of organization, sector, product and technology considered.

The full implementation of a societal perspective in research and innovation, as it is proposed by the RRI concept, it is a long process. It requires the development of appropriate models and methodologies, increase of awareness on the benefits and added value of such approach, and overall a strong cooperation amongst the different actors (research, business, policy and society) toward a common goal of using research and innovation to address societal challenges.

WS5 KN06

The role of sustainability in the manufacture and use of catalysts

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Clariant's innovative catalysts and adsorbents deliver sustainable value to customers by enabling higher production throughput, and lower energy consumption, while reducing hazardous emissions from industrial processes and combustion engines.

Clariant has implemented a sustainability program that looks not only at our production processes, but much more broadly at our responsibility towards human beings and the world we live in. We are conscious that we can make a difference to the health of our planet. Starting from this focus point, we actively work to improve our production processes and make products that can play a crucial role in the creation of more sustainable value chains.

We will explain our efforts in:

- The catalyst preparation process, where we aim for using a high level of recycled materials (such as utilities) with minimum scrap and waste;
- The recycling of spent catalysts;
- Alternative catalyst recipes development, where we substitute critical metals such as Cr(VI);
- Development of new catalysts that enhance process efficiency and save energy and raw materials.

WS5 - Oral Communications

- **WS5-OR01 -** M. Saviano (UNISA) “The Strategic Role of Chemistry in Developing Innovative Health Products for Sustainability: A Science-Policy-Industry Helix Model”
- **WS5-OR02 -** M. Vannini (UNIBO) “Insights into the synthesis of PEF from FDCA: steps toward environmental and food safety excellence in packaging applications”
- **WS5-OR03 -** D. Smacchia (VINAVIL) “Substitution of SVHC: an alternative to PFOA and its derivatives for textile finishing products”
- **WS5-OR04 -** C. Graiff (UNIPR) “Cellulose nanocrystals from waste paper, mixed with silver nanoparticles, as reinforcing agent with biocidal activity for paper preservation”
- **WS5-OR05 -** F. Taddeo (UNINA) “Esters from pelargonic acid and their application as green solvents for printing inks”
- **WS5-OR06 -** G. Grillo (UNITO) “Multi-stage ultrasound-assisted extraction of tea process-residues: a kinetic approach”
- **WS5-OR07 -** F. Matteucci (DHITECH) “The importance of the ecosystem of innovation within water treatment technologies development”
- **WS5-OR08 -** E. Meloni (UNISA) “Soot abatement from biomass boilers by means of open-cell foams filters”
- **WS5-OR09 -** E. Paone (UNIFI) “Transfer hydrogenation of alkyl levulinates promoted by a ZrO2 catalyst: a comparison of batch vs continuous gas-flow conditions”
- **WS5-OR10 -** D. Bonincontro (UNIBO) “Nanosized NiO supported Au-based NPs for the base-free HMF oxidation”
- **WS5-OR11 -** R. Esposito (UNINA) “Transesterification of levulinic acid catalyzed by a µ-oxo-dinuclear iron(III) salen complex”
- **WS5-OR12 -** M. Ricciardi (UNISA) “Catalytic conversion of bio-glycidol into value-added products”
- **WS5-OR13 -** J. De Maron (UNIBO) “Innovative bifunctional catalytic system for methyl methacrylate synthesis: the peculiar role of gallium”

WS5 OR01

The Strategic Role of Chemistry in Developing Innovative Health Products for Sustainability: A Science-Policy-Industry Helix Model

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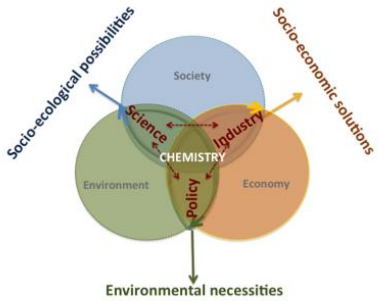
Sustainability is among the key global issues that call for synergistic collaboration between multiple actors. Agreeing on the need of effective Science-Policy (1) and Science-Industry (2) collaboration to address sustainable innovation (2), this work discusses the necessity "to catalyze the mutual interaction between idea and innovation, starting from new, more effective, modalities of communication between Industries, Research and Society" (3). Using the Triple Helix of Sustainability (Fig. 1) as a reference model (4, 5), the study highlights the key role of science in promoting effective Science-Policy-Industry interaction to produce *sustainable* innovation (6) and the centrality of Chemistry as "the solution for the sustainable growth" (3).

Fig. 1 – The Triple Helix of Sustainability (Source: Adapted from 4)



The model highlights the fundamental role of science as a bridging actor between policy and industry and the strategic role of Chemistry, as a "central science" (5), in leading innovation processes for sustainability. An example of effective science-led innovation for sustainability is provided with reference to a multidisciplinary research study on agro-food wastes and by-products e.g. Hazelnut Shells (HS), Roasted Hazelnut Skins (RHS) and Chestnut Spiny Burs (CSB) to design and develop new stable and bioactive particle powder systems as ingredients for pharmaceutical, nutraceutical and food industry (6, 7, 8). Extraction and chemically and biologically studies of the wastes showed interesting composition in antioxidant, antimicrobial and chemopreventive constituents. The extracts were loaded and carried in natural-based polymeric matrix by spray-drying. The produced microsystems were used as bioactive ingredients in oral and topic formulations or in edible films, produced by casting technique, for food packaging. The development of active ingredients based on plant wastes and by-products combined with biodegradable and biocompatible polymers with coating or film-forming ability, appears an attractive approach for the up-cycling and valorisation of wastes addressing the formulation of health (pharmaceutical or nutraceutical) products and/or films able to preserve quality and safety of food. The study highlights how effectively chemistry can help companies to develop innovations that combine positive environmental, social and economic impacts.

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WS5 OR02

Insights into the synthesis of PEF from FDCA: steps toward environmental and food safety excellence in packaging applications

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Poly(ethylene 2,5-furandicarboxylate) (PEF) is considered today as a very promising biobased polymer for packaging applications. The main reason lies in its extraordinary barrier properties: oxygen permeability in PEF is reduced by a factor of about 10 with respect to poly(ethylene terephthalate) (PET) (1). In terms of the synthesis of PEF, scientific literature describes synthetic procedures based on the transesterification of the dimethylester of the 2,5-furandicarboxylic acid (2,3,4). This research, instead, aims at studying the possibility of a practical and profitable synthetic route of PEF starting from the 2,5-furandicarboxylic acid. In this respect two catalysts, zinc acetate (ZnAcO) and aluminum acetylacetonate ($Al(acac)_3$), chosen for their compatibility with food contact applications and for featuring a potentially reduced environmental impact, were investigated. The synthesis was performed by using tight reaction conditions: low excess of diol and short reaction time. Indeed, the use of high amount of glycol could lead to the ether-bridges (DEG) formation, which significantly reduces the extremely valuable barrier performances of PEF; high polymerization times lead to material yellowing, indicating the occurrence of by-side reactions. Different catalyst amounts and addition times were tested and the obtained polymers were characterized in terms of inherent viscosity, color (absorbance at 400 nm), and diethylene glycol content, as summarized in Table 1. Since titanium (IV) butoxide (TBT) is the most used catalyst in the PEF syntheses, PEF samples prepared with it were reported as a reference for the present study.

Table 1: Characteristics of PEF samples prepared with different catalysts added in the first stage

Catalyst	Amount of catalyst (ppm)	η (dl/g)	Absorbance	DEG (mol%)	Tg (°C)
TBT	400	0.36	0.53±0.03	4.7	82
TBT	50	0.32	0.35±0.01	5.0	83
ZnAcO	400	0.34	0.15±0.00	3.7	84
ZnAcO	50	0.25	0.12±0.00	2.7	84
$Al(acac)_3$	400	0.19	0.07±0.01	3.2	80
$Al(acac)_3$	50	0.25	0.07±0.01	3.3	83

Results show that ZnAcO and $Al(acac)_3$ are very promising catalysts for the PEF polymerization from FDCA, because the use of ZnAcO allows them to reach relatively high inherent viscosity in the usual polymerization procedure, while the use of $Al(acac)_3$ leads to materials characterized by very low yellowing. In this case, the moderate molecular weight obtained for aluminum-based PEF was overcome by a final step of solid state polymerization (SSP), which increases the viscosity from 0.25 to 0.39 dL/g in just 3 days. Finally, the obtained amorphous PEF samples result filmable and therefore suitable for the manufacturing of various packaging articles.

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WS5 OR03

Substitution of SVHC: an alternative to PFOA and its derivatives for textile finishing products

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Starting from 4th of July 2020 perfluorooctanoic acid (PFOA) and its salts shall not be manufactured or placed on the market as substances on their own. It means that PFOA and any related substance (including its salts and polymers) having a linear or branched perfluoroheptyl or perfluorooctyl group directly attached to another carbon atom, as one of the structural elements shall not, from 4 July 2020, be used in the production of, or placed on the market in: another substance, as a constituent; a mixture; an article, in a concentration equal to or above 25 ppb of PFOA including its salts or 1000 ppb of one or a combination of PFOA-related substances (1).

The substance was proposed to be identified as a substance meeting the criteria of Article 57 (c) of the REACH regulation by the German Federal Institute for Occupational Safety and Health (BAuA) on March 2013. The proposal concludes that PFOA should be classified as toxic for reproduction category 1B in accordance with the CLP Regulation. It was also proposed to identify the substance as persistent, bioaccumalative and toxic (PBT) according to Article 57 (d) (2).

From 1951 until 2004 the estimated total global production was 3600-5700 t PFOA and its ammonium salt APFO (3). APFO is mainly used as a processing aid in the production of fluoropolymers and fluoroelastomers. Fluoropolymers are high performance plastic materials and fluoroelastomers are high performance synthetic rubbers, especially in terms of hydrophobicity, high lipophobicity and flame resistance. Residues from production, processing and use of fluorinated polymers are suspected in several industries, above all textile finishing, electroplating and paper industry. In general, perfluorinated compounds (PFCs) with eight carbon atoms can be replaced with shorter chain fluorinated chemicals containing six or less carbon atoms, with a severe reduction of the previously mentioned properties. Non-fluorinated alternatives are available as well, i.e. propylated aromatics (naphthalene or biphenyls) and aliphatic alcohols (sulphosuccinate and fatty alcohol ethoxylates) (4).

Vinavil S.p.A., a subsidiary of Mapei group, is one of the Italian leading company in the manufacture of water-based polymer dispersion based on vinyl acetate, vinyl acetate-ethylene copolymers, acrylics and styrene/acrylics copolymers that find use in a wide number of sectors such as adhesives, coatings, building and construction, and textile. Since many years, Vinavil S.p.A. has committed itself in providing a significant contribution for a sustainable world and in this perspective has recently launched a campaign, followed by several initiatives, with the intent to replace all the as SVHCs (substances of very high concern).

Currently the main efforts are focused on the replacement of formaldehyde in Vinavil polymer emulsions as well as to find valuable technical alternatives to the perfluorinated compounds. It will be discussed how the R&D department of Vinavil S.p.A. is dealing with the of PFCs substitution from textile finishing products, especially in the field of treatments for high technical fabrics (e.g. winter sports clothes).

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WS5 OR04

Cellulose nanocrystals from waste paper, mixed with silver nanoparticles, as reinforcing agent with biocidal activity for paper preservation

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In this work, aqueous suspensions of cellulose nanocrystals obtained by waste paper recycling, were selected as nanoscale constituents of reinforcing agents for Whatman paper.

Cellulose nanocrystals dispersed in water were obtained in good yields by sulfuric acid hydrolysis starting from waste paper. XRD analysis on cellulose nanocrystalline powder showed high crystallinity index (1). The aqueous suspensions were used as such and mixed with silver nanoparticles, obtained by treating $AgNO_3$ with $NaBH_4$ at room temperature, in order to give biocidal activity to the reinforcing treatment on paper samples. TEM images evidence the presence of elongated fibers of nanocellulose, with length in the 100-150 nm range, together with small silver nanoparticles dispersed uniformly in the mixture. The average silver nanoparticle size is 5-25 nm.

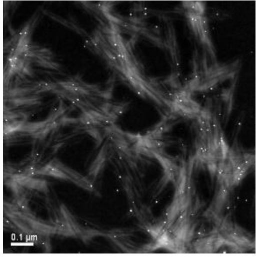

Fig. 1. TEM image of CNC/nAg

The samples were prepared depositing the suspensions by brush. The *tensile strength* (maximum tensile force before rupture, kN/m) and the *tensile stretch* (the relative maximum elongation before rupture) have been measured for the untreated and treated Whatman paper samples in both the principal directions of the paper sheet. The *tensile strength* is not significantly affected by the reinforcing treatments, while the maximum *stretch* before rupture increases about 35-40%, both in longitudinal and perpendicular directions.

Antibacterial activities against *Escherichia coli* and *Bacillus subtilis* have been investigated: the mix of CNC/nAg shows a very good antibacterial effect.

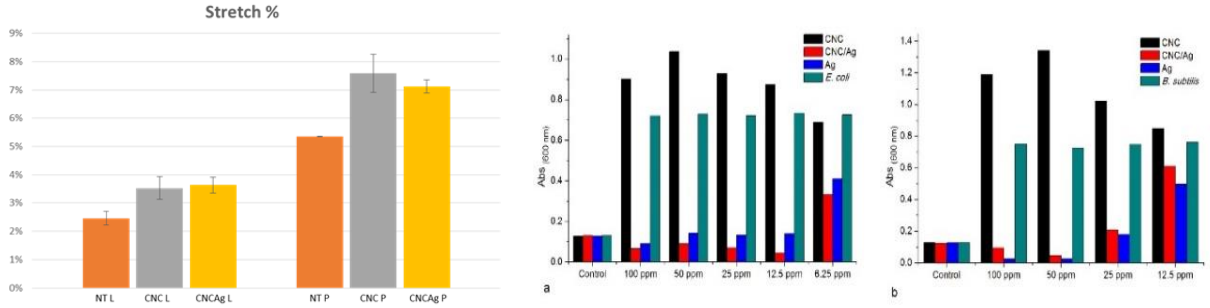

Fig. 2. (Left) Relative maximum elongation for not treated paper, CNC and CNC/nAg treated paper samples (L = longitudinal, P = perpendicular). (Right) (a) Growth of *E.coli* and (b) *B.subtilis* in the presence of CNC, a mix of CNC/nAg and nAg alone at different concentrations for MIC determination

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WS5 OR05

Esters from pelargonic acid and their application as green solvents for printing inks

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Esters are generally used as plasticizers, solvents, flavor chemicals and as precursors for pharmaceuticals, agrochemicals and other fine chemicals. Esterification of carboxylic acids with alcohols is commonly catalyzed using soluble acids. These catalysts are characterized by high activity, but they show several negative aspects, such as their corrosive nature, the existence of side reactions and they cannot be easily separated from the reaction mixture. The commercial cation-exchange resin, Amberlyst 15, represents an important alternative, as it can be easily removed from the liquid mixture after the reaction, it is not corrosive to the equipment and the side reactions can be almost completely suppressed (1). Among carboxylic acids, pelargonic acid has a great importance as it can be obtained from vegetable oils. Benessere et al. (2) demonstrated the possibility of using pelargonic acid esters as solvents for bio–based varnishes in combination with a commercial resin. The obtained solvents showed an excellent ability to disperse resins derived from rosin in unprecedented mass percentage, in shorter time and at lower temperature with respect to commonly used solvents. Sharma et al. (3) investigated the esterification of pelargonic acid with methanol with homogeneous catalysts and heterogeneous ones.

In the present work, a kinetic study was conducted using both homogeneous (H_2SO_4) and heterogeneous catalyst, using 2-ethyl-1-hexanol as alcohol in a batch reactor. A loop reactor made by a stirred jacked steel batch reactor connected to a packed bed reactor in which there is the heterogeneous catalyst will be used to validate the kinetics.

Acknowledgements

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WS5 OR06

Multi-stage ultrasound-assisted extraction of tea process-residues: a kinetic approach

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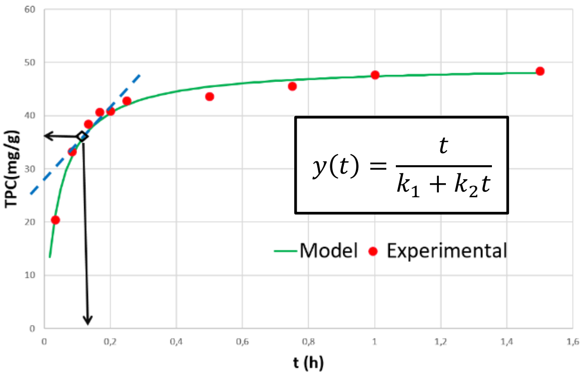
Tea (*Camellia Sinensis*), with a production of 5.45 mln tons/year, is the most common beverage in the world, with related huge processing wastes. (1) In the lasts decades, healthy effects of tea-based products gained great attention (antioxidant and chemopreventive properties) (2), thanks to the bioactive polyphenolic fraction, mainly composed by catechins and phenolic acids (3). This interest has been merged with the industrial hot topic of new sustainable processes design, focusing on large production rates. Ultrasound-assisted extraction (UAE), among the enabling technologies, is recognized as an elective technique for a fast and efficient recovery of polyphenols at room temperature. (4)

In this work, tea leaves residues, provided by manufacturers, were extracted in simple water using a cup horn system (24 kHz, 200 W). By means of Folin-Ciocalteau essay, Total Phenolics Compounds (TPC, gallic acid equivalents) were measured on isolated extracts, outlining the process extraction rate.

The kinetic profile has been described by the Peleg hyperbolic model (Fig.1), extrapolating kinetic constants and verifying the equation fitting via parametrical linearization.



$$y(t) = \frac{t}{k_1 + k_2 t}$$

Fig.1: *Extraction kinetic – model and experimental*

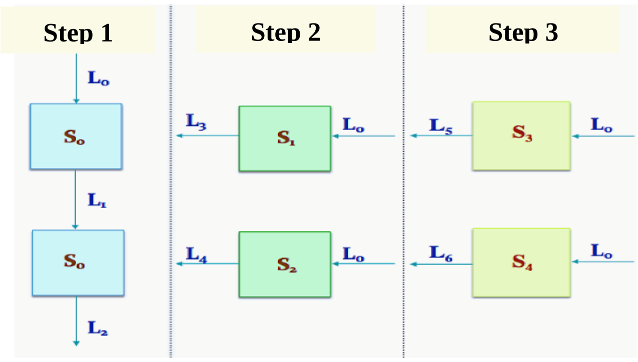


Fig.2: *Cross-flow extraction scheme [3 steps - 2 batches]*

The collected data array enables the design of a cross-flow UAE protocol (Fig.2), leading to isolate an enriched polyphenolic fraction and to complete matrix depletion.

The final product was characterized by antioxidant activity (DPPH essay), LC-MS and HPLC analysis. Each result was compared to a conventional benchmark.

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WS5 OR07

The importance of the ecosystem of innovation within water treatment technologies development

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Water treatment technology deals with the removal of impurities present in water during its use or storage and convert it into usable form. Global water treatment industry, whose market size was valued approximately 145 bln$ in 2015, is expected to witness significant growth in the coming years (CAGR 4,1% from 2015 to 2022), owing to the rise in awareness about water scarcity, growth in innovations in water treatment technologies, investments by key market players and government in R&D in this sector. Major challenges for water treatment technology market include the decrease of equipment costs, the increase of personnel expertise and the capability of applying the waste mining approach to the plants (1). The overcoming will be possible thanks to technological advancements and vigorous R&D activities. The combination of the two will be possible in an ecosystem of innovation where all the actors try to share their knowledge using an open innovation approach.

The presentation will discuss a case where the Apulian ecosystem of innovation acted to develop Advanced Oxidation Processes applied to water treatment. More in details, it will be shown the role of chemistry in the abatement of emerging contaminants within water treatment plants thanks to the combination of nanostructured photocatalysts and UV technology. After presenting the water treatment challenges, the team expertise and the different actors/partners, it will be explained the scientific/technological research. The author will show how important was, in order to finalize the process of innovation, the implementation of a multi-language and customized approach to develop the network and the different interactions among the actors – technical, commercial, legal, social and financial (2). It will be explained the catalyzing effect within the process of innovation of public funds for R&D, the importance of demonstration projects - verifying technologies on one hand and creating a first commercial market on the other (3), and the role of intermediary of knowledge institutions - organizational structures that stimulate the innovation process through a multilingual approach (4). In conclusion, after having shown a best practice (getting a big win onboard approach (5)), the presentation will try to stimulate the discussion on how to overcome the European paradox - the perceived failure of European countries to translate scientific advances into marketable innovations.

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WS5 OR08

Soot abatement from biomass boilers by means of open-cell foams filters

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Currently, fossil fuels such as oil, coal and natural gas represent the main energy sources in the world. However, it is well known that these sources of energy will deplete within the next years (1). So, due to increasing environmental concerns especially related with the use of these fossil fuels, new solutions to limit the greenhouse gas effect are continuously sought. Among the available alternative energy sources, including hydro, solar, wind etc. to mitigate greenhouse emissions, biomass is the only carbon-based sustainable option (2). However, despite an environmentally friendly use of renewable energies, incomplete combustion of biomass can lead to the emission of environmental pollutants as well as substances which are hazardous to health (3). In comparison to gaseous and liquid fossil fuels, the emissions of particulate matter (PM, or soot) are higher, leading to concerns about the availability of cost-effective techniques to reduce emissions in biomass combustion plants: so, filtration devices are mandatory. Different filtration systems are today available; some have reached a technological maturity and a consequent wide diffusion while others, though promising, have not yet demonstrated adequate features to be considered competitive. In the first class there are electrostatic precipitators, sleeve filters and wet scrubbers, which are standard solutions in medium to large plants. In the second class there are ceramic filters which in principle can be applied both in new equipment and in retrofit of existing boilers and may be easily scaled according to the size of the boiler. In our previous works we studied the use of catalytic ceramic wall flow filters as soot emission control devices of biomass-fired boilers and stoves (4). Starting from those results, in this work we investigated the use of a different kind of filters, the open-cell ceramic foams, characterized by a different porosity if compared to wall flow filters. The filters were tested in a customised sampling line at the exhaust of a 30 kW pellets boiler, and regeneration was specifically obtained by a high-temperature electrical heater. PM concentration in the flue gas was monitored by means of a real-time continuous detector and a cascade impactor. The tests evidenced that the higher average pores diameter of the foams, compared to ceramic wall-flow filters, resulted in two main consequences, (i) lower pressure drop, and (ii) lower filtration efficiency. In particular these results are very important, since the pressure drop never reached a critical value for the normal biomass boiler functioning, and the filtration efficiency is always higher than 50%: in this way this solution could be a feasible device for soot emissions control. Further studies are still running to investigate the deposition of a catalyst on ceramic foams.

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WS5 OR09

Transfer hydrogenation of alkyl levulinates promoted by a ZrO_2 catalyst: a comparison of batch vs continuous gas-flow conditions

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Levulinic acid (LA) is considered one of the 12 bio-based molecules that could potentially replace petroleum-based chemical building blocks (1), and since it can be easily obtained, in a single-step hydrolysis process, from cellulose, it is surely one of the most promising future building blocks of the biobased chemical industry (2).

In the last years, together with LA, alkyl levulinates have been successfully used as starting feedstocks for the preparation of GVL generally used as flavoring agent in food industry, as green solvent, as intermediate in the fine chemicals synthesis and as starting material for the production of bio-based polymers and resins. The use of alkyl levulinates in GVL preparation has attracted great industrial interest thanks to their lower boiling point and free acid characteristics, as compared to LA.

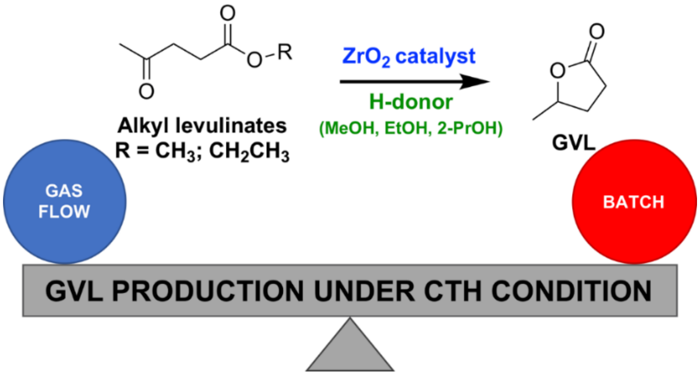
Together with traditional hydrogenation conditions, catalytic transfer hydrogenation (CTH) reactions has gained a lot of research attentions (3, 4). In this regard, ZrO_2 seems to be one of the most active and selective catalysts in the CTH of LA and its esters to GVL. In this context, we compare the performance of a tetragonal ZrO_2 catalyst in the transfer hydrogenation of methyl and ethyl levulinate, in both continuous gas-flow and batch conditions.

ZrO_2 catatlyst was prepared by using the precipitation method and fully characterized by BET, XRD, NH_3 and CO_2-TPD, in-situ DRIFT, DTA and TGA analysis.

Under batch conditions, the product selectivity in liquid phase was found to be dependent on the choice of the H source. On using 2-PrOH as H-donor, a very high selectivity to GVL was observed, whereas reactions carried out in EtOH and MeOH were found to be by far less efficient.

On the other hand, under continuous gas-flow conditions, high conversions and GVL yield can be obtained using 2-PrOH and EtOH while a poor reactivity with MeOH was observed. Moreover, the ZrO_2 catalyst shows an excellent stability for more than 10 hours of time of stream and can be easily regenerated *in-situ* by feeding air at 400°C for 2 h.

The competitive processes were found to be the transfer hydrogenation, ruled by the ability of alcohols as reducing agents, and the transesterification strongly influenced by the steric hindrance of the H-donor molecule.



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WS5 OR10

Nanosized NiO supported Au-based NPs for the base-free HMF oxidation

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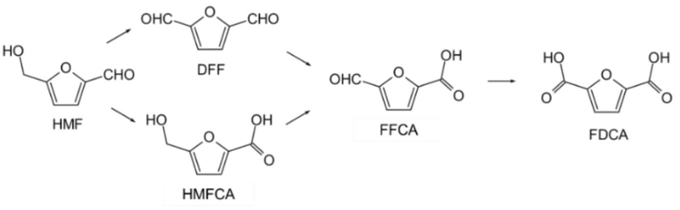

Figure 3 HMF oxidation pathways and reaction network

The depletion of fossil-derived resources and the need to decrease the emission of green-houses gases led scientists to look for sustainable materials to replace the already existing ones. For instance, 2,5-furandicarboxylic acid (FDCA) has been identified as the bio-derived counterpart of terephthalic acid for the synthesis of polyesters. In fact, FDCA could be obtained by means of selective oxidation of 5-hydroxymethylfurfural (HMF), a bio-derived platform molecule produced by glucose hydrolysis. HMF oxidation (Fig. 1) is usually performed in a batch reactor, using water as solvent, oxygen as oxidant and supported metal nanoparticles (NPs) as the desired catalysts. Supported Au NPs and Au-Pd NPs have been found to be suitable catalysts in the conversion of HMF into FDCA (1) at mild reaction conditions, but the presence of inorganic bases (e.g. NaOH) is needed to produce FDCA at high yield. Recently, it has been demonstrated the possibility of oxidizing aromatic and aliphatic alcohols under base-free conditions using metal supported nano-sized nickel oxide (nNiO) catalysts (2).

In the present study, we report for the first time the catalytic performance of supported Au and Au-Pd NPs (Au:Pd metal molar ratio equal to 6:4) on nNiO in the liquid-phase oxidation of HMF under base-free conditions.

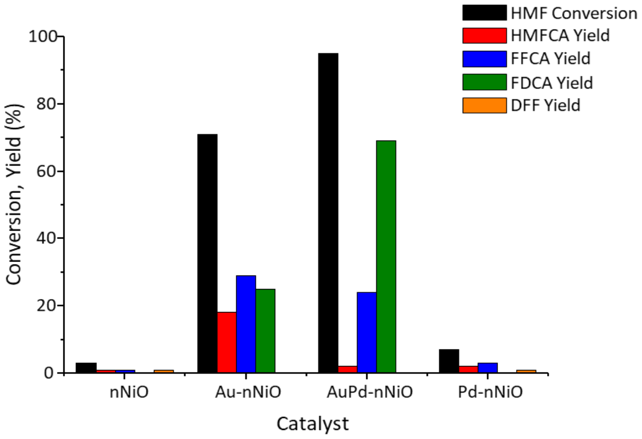

Figure 4 HMF conversion and product yields for Au-based nNiO catalysts. Reaction conditions: 90°C, 6h, 10bar O_2.

The oxidation of HMF performed in the presence of the bare nNiO demonstrated the inability of the support to catalyze the reaction. On the contrary, the results obtained using Au-nNiO catalyst demonstrated that, even without the addition of the base, HMF was converted (71 %) after 6h of reaction with 25% of yield in FDCA. The preparation of a bimetallic AuPd system (called AuPd-nNiO) led to a significant increase of the activity (95% of HMF conversion and 69% FDCA yield), confirming that the alloyed bimetallic structure enhances catalyst performance as already reported for other supports (1). Pd-nNiO did not show any relevant catalytic activity. We performed detailed mechanistic studies and analysis of the spent catalyst and we found that DFF, one of the main intermediates, has a poisoning effect on the performance of Au-nNiO catalyst, which is avoided by using the alloyed AuPd-nNiO catalyst. In conclusion, a novel environmentally benign route to FDCA has been successfully designed, using highly active and stable supported Au-Pd alloyed nanoparticles on nNiO under base- free conditions.

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WS5 OR11

Transesterification of levulinic acid catalyzed by a μ-oxo-dinuclear iron(III) salen complex

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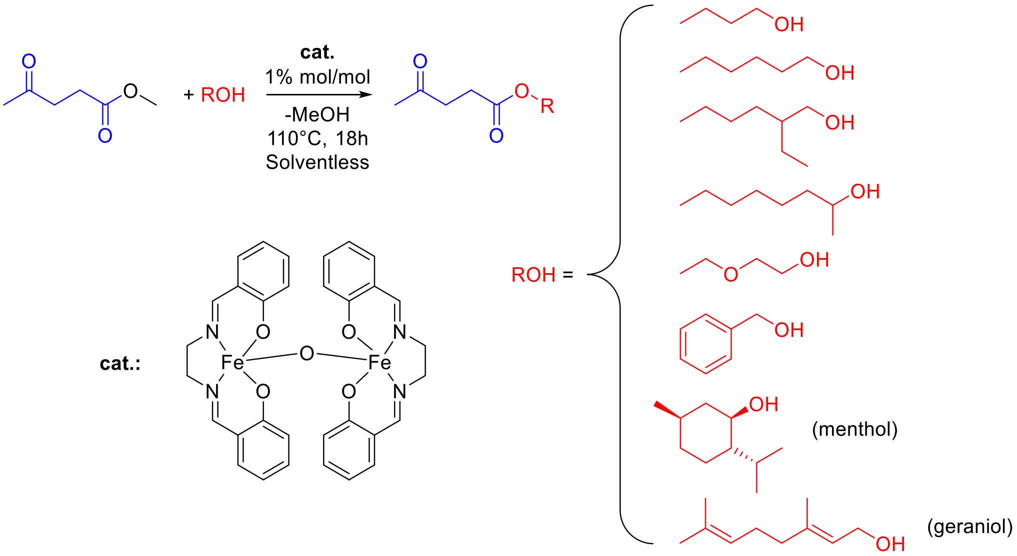
Renewable sources of raw materials are needed and substituting the old fossil-fuel derived with new biomass derived is a priority.

Levulinic acid is a very convenient starting material because (1):

- it can be obtained for degradation of cellulose or amid based biomass.
- it has two functional groups, a carboxylic acid and a ketone, that can be used to convert it in a variety of chemicals.

At the same time, esters are widely used in many industrial fields, from cosmetics to plasticizers and solvents.

In this work, a variety of esters of levulinic acid are prepared through a reaction of transesterification of methyl levulinate, and are obtained in good yields, mild conditions and without the use of auxiliary chemicals. The chosen catalyst is a μ-oxo-dinuclear iron(III) salen complex (cat. in scheme 1) that acts as a Lewis acid catalyst, and already showed promising results in transesterification reactions.(2)



Scheme 1 - Transesterification of methyl levulinate and catalyst used.

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WS5 OR12

Catalytic conversion of bio-glycidol into value-added products

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The present work is focused on the catalytic conversion of bio-glycidol into value-added products.
Bio-glycidol (2,3-epoxy-1-propanol) is obtained from 2-chloro-1,3-propanediol, produced as waste during the Epicerol® process, that represents one of the most consolidated bio-based industrial process able to convert glycerol into epichlorohydrin. (1)
Glycidol, in turn, is successfully employed as starting material to produce glyceryl ethers, propanediols and glycerol ketals.
Homogeneous and heterogeneous Lewis and Brønsted acids were used as catalysts for the etherification of glycidol by ring opening reaction with an alcohol as nucleophile. As a matter of fact, commercial metal salts (chlorides and triflates of Fe, Al, Bi and Zn) were tested as homogeneous catalysts giving promising results in term of the catalytic activity in the case of metal triflates. (2,3)
Moving to heterogeneous catalysts, sulfonated resins, metal triflates and sulfonic groups supported catalysts were employed in the synthesis of glycerol monoethers, achieving good results.
The proposed synthetic route can be applied to several alcoholic substrates ranging from short chain to long chain alcohols, obtaining precious compounds in high yield. (4)
Considering the hydrogenolysis reaction of glycidol, instead, a system formed by the combination of Amberlyst 15 and palladium on carbon was used as catalyst. An acid resin such as Amberlyst 15 can act as co-catalyst in the hydrogenolysis thanks to its property to activate the epoxide ring towards the ring opening reaction. The amount of this resin and the solvent medium were optimized in order to reach total selectivity towards 1,2-propanediol. (5)
Lastly, several acid heterogeneous catalysts, both commercially available and synthetic, were tested in the ketalization reaction of glycidol with acetone, producing solketal under mild reaction conditions. The best catalytic system, under optimized conditions, was selected for the production of other glycerol ketals using different ketones as starting material. (6)
Furthermore, life cycle assessment (LCA) analyses were used as a tool to evaluate the environmental sustainability of the proposed synthetic processes, comparing them with those reported in literature.

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WS5 OR13

Innovative bifunctional catalytic system for methyl methacrylate synthesis: the peculiar role of gallium

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Methyl methacrylate (MMA) is the monomer for polymethyl methacrylate manufacture. The state of art in MMA production is the Alpha process (1) which employs formaldehyde (FA) for the hydroxy-methylation/dehydration of methyl propionate (MP), the latter produced by ethylene hydroformylation in the presence of methanol (MeOH). In order to achieve a more sustainable MMA manufacture, MP should be produced from bio-based platform molecules such as 1,2-propanediol (2) avoiding the utilization of FA (known carcinogen) in favor of a one-pot approach which consists in its *in-situ* production by MeOH dehydrogenation. The one-pot reaction between MeOH and MP in the gas phase has been investigated by few authors (3,4) over catalysts possessing basic/redox features: the redox properties are required to dehydrogenate MeOH to FA, while the basicity is required to abstract an alpha-proton from MP and activate it to nucleophilic attack on the aldehyde. Since basic catalysts are known to catalyze MeOH dehydration at high temperatures (5), preliminary studies have been conducted with pure MgO: the main reaction in the temperature range 350-450°C is ketonization which produces 3-pentanone (3-P), CO_2 and MeOH. Alpha-protons in 3-P are more acidic and in higher number in respect to MP and therefore it reacts faster with FA, producing also mono- and di-methyl-pentenones. At 500°C MgO become much more active for MeOH dehydrogenation and hydroxy-methylation but the desired product is never obtained with satisfying yield due to consecutive H-transfer reactions which transform MMA into methyl isobutyrate (MIB), methacrolein (MA), isobutyraldehyde (IBA), 2-methylpropanol (2-MP) and isobutylene (the latter is formed from 2-MP dehydration). The poor catalytic result obtained over MgO suggest that an effective catalyst should possess a strong dehydrogenating activity at low temperatures in order to produce a large excess of FA to minimize ketonization and H-transfer. Starting from this hypothesis we investigated the catalytic activity of two post-transition metal oxides possessing redox features (namely Ga_2O_3 and SnO_2) and found that both catalysts are more active than MgO in MeOH dehydrogenation at low temperatures and less active in both ketonization and H-transfer. Best results were obtained with Ga_2O_3, which has been chosen to develop some bifunctional catalysts introducing Ga(III) into MgO; on the basis of our results so far, the best one is the Mg/Ga/O mixed oxide with a Mg/Ga molar ratio of 10 (MP conversion = 34%, MMA selectivity=24%). The presence of Ga not only enhances the catalyst dehydrogenating properties at low temperatures (300-350°C) leading to higher yields in FA and H_2 but also reduce ketonization to an extent that makes it almost negligible. Indeed, the reaction by-products (MIB, IBA, MA, 2-MP and isobutylene) are those deriving from H-transfer reaction. Finally, combining characterization technics and catalytic results we were able to determine the reaction scheme and minor/major reaction pathways, and assess structure-activity relationships.

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WS5 - Poster Communications

- **WS5 PO01 -** Giulia Balestra, Stefania Solmi, Tommaso Tabanelli, Fabrizio Cavani *“Sustainable bio-products: study of the catalytic hydrogenation of 5-(hydroxymethyl)furfural”*
- **WS5 PO02 -** Federico Bella, Lucia Fagiolari, Claudio Gerbaldi *“Ambient condition fabrication of perovskite solar cells: towards industrial approaches”*
- **WS5 PO03 -** Alice Cappitti, Antonella Salvini, Alessandra Papacchini, Donatella Giomi, Brunella Perito *“Synthesis, characterization and application study of nanocomposites”*
- **WS5 PO04 -** Silvia Giorgi, Fabio Chiozza, Fabrizio Bernardini, Antonella Salvini *“Crosslinkers for polyvinyl alcohol-based formulations”*
- **WS5 PO05 -** Simone Maranghi, Maria Laura Parisi, Riccardo Basosi, Adalgisa Sinicropi *“Methodologies for the sustainability evaluation of novel chemical products for innovative renewable energy technologies”*
- **WS5 PO06 -** Nicole Mariotti, Matteo Bonomo, Marco Zanetti, Gabriele Ricchiardi, Marcello Baricc, Claudia Barolo_*“Increasing sustainability of materials for renewable energy”*
- **WS5 PO07 -** Eugenio Meloni, Bruno Rossomando, Ivan Arsie, Cesare Pianese, Vincenzo Palma_*“Regeneration tests of a catalytic DPF at the exhaust of a common-rail diesel engine”*
- **WS5 PO08 -** Raffaella Mancuso, Rossana Miliè, Ida Ziccarelli, Bartolo Gabriele *“Carbonylative Regio- and Stereoselective Synthesis of (Z)-2-(2-Oxopyrrolidin-3-ylidene)acetates”*
- **WS5 PO09 -** Maria Ricciardi, Raffaele Cucciniello, Francesco Della Monica, Carmine Capacchione, Antonio Proto_*“A new [OSSO]-Fe(III) triflate complex as catalyst for the regioselective ring opening of glycidol to monoalkyl glyceryl ethers”*
- **WS5 PO10 -** Maria Ricciardi, Raffaele Cucciniello, Daniele Cespi, Fabrizio Passarini, Joel Barrault, Carmine Capacchione, Antonio Proto *“Production of value-added chemicals starting from glycidol as green feedstock”*
- **WS5 PO11 -** Carmelina Rossano, Vincenzo Russo, Rosa Vitiello, Rosa Turco, Riccardo Tesser, Martino Di Serio *“Kinetics of the Amberlite IR-120 catalyzed acid esterification of ethanol with levulinic acid”*
- **WS5 PO12 -** Vincenzo Russo, Ferdinando de Luca Bossa, Riccardo Tesser, Maria Oliviero, Martino Di Serio, Letizia Verdolotti *“Bio-based Rigid Polyurethane foams from renewable resources”*
- **WS5 PO13 -** Annalisa Sacchetti, Irene Tosi, Tommaso Tabanelli, Fabrizio Cavani, Anders Riisager *“Effect of mesoporous zeolites for the selective conversion of carbohydrates into methyl lactate”*
- **WS5 PO14 -** Antonella Salvini, Alessandra Papacchini, Alice Cappitti, Donatella Giomi *“Production of green polymeric formulations from natural and renewable sources”*
- **WS5 PO15 -** Michela Signoretto, Elena Ghedini, Federica Menegazzo, Pietro Riello, Silvia Tabasso, Giorgio Grillo, Giancarlo Cravotto_*“Hi-tech cosmetics by cocoa and black tea extracts: a valuable synergy of technologies to transform waste in high value products”*
- **WS5 PO16 -** Tommaso Tabanelli, Carlo Giliberti, Rita Mazzoni, Raffaele Cucciniello, Fabrizio Cavani *“Glycerol carbonate as an innovative alkylating agent for phenolics”*
- **WS5 PO17 -** Riccardo Tesser, Rosa Turco, Vincenzo Russo, Rosa Vitiello, Martino Di Serio *“Bio-lubricants Synthesis from the Epoxidized Oil promoted by Clays: Kinetic modelling”*

- **WS5 PO18 -** Sebastiano Tieuli, Michela Signoretto Federica Menegazzo, Riccardo Pasquale, Massimiliano Silvestri *“"GOAST"- Green Organic Agents for Sustainable Tanneries”*
- **WS5 PO19 -** Rosa Turco, Martino Di Serio, Riccardo Tesser, Massimo Fagnano, Mario Malinconico, Salvatore Mallardo, Gabriella Santagata *“Evaluation of Cynara Cardunculus Biomass Recovery as an Eco-Sustainable Resource for Bioplastics Bioplasticizers”*
- **WS5 PO20 -** Rosa Vitiello, Vincenzo Russo, Rosa Turco, Francesco Taddeo, Riccardo Tesser, Antonio Buonerba, Alfonso Grassi, Martino Di Serio *“Sustainable base-lubricant synthesis using heterogeneous catalysts”*
- **WS5 PO21 -** Dafne Cimino, Francesco Enrichi, Elti Cattaruzza, Giancarlo Gasparotto, Alberto Sozza, Enrico Trave, Elisabetta Zendri *“Testing hybrid coatings as protective solutions for outdoor lighting systems to be exported to the Middle-East: an effective factory-university collaboration within the TEMART project”*
- **WS5 PO22 -** Maria Grimaldi, Antonella Cavazza, Claudio Corradini “Innovative material from agro alimentary by-products to realize a spray active packaging in a *context of sustainability and Circular Economy”*
- **WS5 PO23 -** Melissa Greta Galloni, Sebastiano Campisi, Michele Ferri, Antonella Gervasini *“The “virtuous life-cycle of hydroxyapatite”: from removal of heavy metals in polluted wastewaters to new ecofriendly catalysts for air-quality protection”*

WS5 PO01

Sustainable bio-products: study of the catalytic hydrogenation of 5-(hydroxymethyl)furfural

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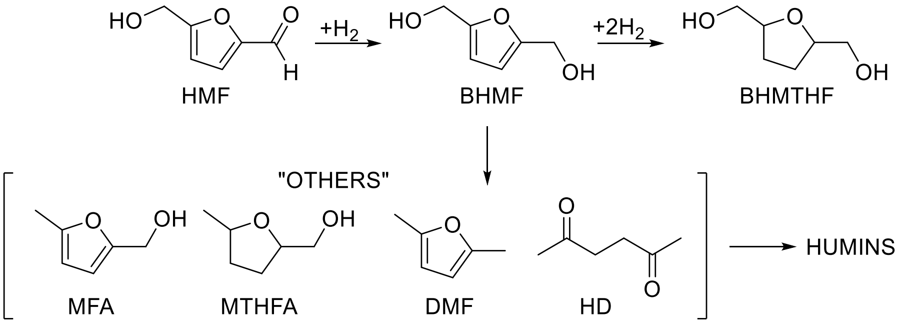
The production of biomass-derived fuels and chemicals is of great importance for the transition to a more sustainable future. In this context, 5-(hydroxymethyl)furfural (HMF) has been identified as a key precursor for the production of biofuels and high added value chemicals. Indeed, the products obtained by hydrogenation of HMF are potential sustainable substitutes for petroleum-based building blocks used in the production of chemicals. (1,2) Among them, the product of the selective reduction of the formyl group of HMF, the 2,5-bis(hydroxymethyl)furan (BHMF), is widely used as an intermediate for the synthesis of resins, fibers, foams, drugs, polymers and crown ethers. The further reduction of the furan ring leads to the formation of 2,5-bis(hydroxymethyl)tetrahydrofuran (BHMTHF), which can be used as green solvent and monomer. (2) Moreover, the hydrogenolysis of HMF generates 2,5-dimethylfuran (DMF), and from its consecutive hydrogenation it is possible to obtain 2,5-dimetiltetrahydrofuran, both are promising bio-fuel additives. (1) In this work, the catalytic hydrogenation of HMF has been investigated over three supported Pd heterogeneous catalysts. Two of them were made of palladium supported on carbon with different metal loadings, 1 and 10 wt%, both being commercial samples. The catalyst consisting of palladium supported on γ-alumina, Pd/γ-Al_2O_3 1 wt%, was prepared in the lab through the so-called "sol-immobilization" method (3). The reactions were performed in liquid phase using water as the solvent, working in both batch (stainless steel autoclave) and continuous-flow (H-Cube Mini, developed by ThalesNano Inc.) reactors. The effect of the main reaction parameters, such as temperature, hydrogen pressure and reaction time/contact time has been investigated in detail. The obtained results clearly show the importance of the reaction set-up in order to enhance the selectivity toward an intermediate product such as BHMF. Indeed, by working at 90°C and 50 bar of hydrogen over the Pd/C 10 wt% catalysts, the selectivity of BHMF achieved was up to 77% by choosing the optimal contact time in the flow reactor. Some by-products (named "others" in Scheme 1) given by the subsequent hydrogenolysis, hydrogenation and ring opening reactions of the main products were identified in the reaction mixture by GC-MS. According to the results obtained, a reaction pathway that needs future investigation has been proposed (Scheme 1).



Scheme 1. Reaction network proposed for the hydrogenation and hydrogenolysis of HMF in water. (MFA: 5-methylfurfuryl alcohol; MTHFA: 5-methyltetrahydrofurfuryl alcohol; DMF: 2,5-dimethylfuran; HD: 2,5-hexanedione)

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WS5 PO02

Ambient condition fabrication of perovskite solar cells: towards industrial approaches

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The power conversion efficiency of perovskite solar cells (PSCs) has remarkably increased, in just a few years, from 3.8 to 22.7%, due to the excellent properties of organometal-halide perovskite, such as strong and broad optical absorption form visible to near infrared, high electron and hole diffusion length and a low surface recombination velocity (1). Nevertheless, PSCs are susceptible to oxygen and water, because of a degradation pathway leading to the formation of lead iodide, methylammonium and hydrogen iodide. For this reason, perovskite materials require high temperature and glove-box synthetic conditions, thus hindering large-scale applications.

During last year, a few efforts have been made in the development of ambient condition fabrication strategies, such as thermal engineering (2) and the use of anti-solvents (3). In the first case, the substrate TiO_2 is pre-heated at low temperature before spin-coating deposition of perovskite precursors. This ensures phase purity and a pinhole-free morphology, with a PCE reaching 12%. In the second case, the use of anti-solvents reduces the solubility of perovskite precursors, thereby promoting fast nucleation and rapid crystallization. In this way, the effect of air-moisture is less relevant.

In conclusion, the fabrication of PSCs in open air atmospheric conditions is challenging, but necessary for photovoltaic application of perovskite materials (4).

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WS5 PO03

Synthesis, characterization and application study of nanocomposites

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Recently, oligoamides nanocomposites with core-shell structure and potential antimicrobial and antifungal activity were synthesized using functionalized TiO_2 nanoparticles (1). In particular, the nanocomposite TiO_2-polyethylenetartaramide was used to test the antimicrobial activity, showing a good efficacy against fungal attack by *Trametes versicolor* on wood specimens (*Fagus sylvatica*). In fact, the titanium dioxide, contained in this nanocomposite in the crystalline form of anatase, performs an antifungal function, thanks to its photocatalytic activity promoted by electromagnetic radiation with wavelengths in the UV region.

Now, vinyl acetate copolymers were synthesized with a controlled growth on the activated and functionalised TiO_2 nanoparticles. These products can show improved properties in comparison with the single components (TiO_2 nanoparticles or vinyl acetate copolymers), obtaining nanocomposites able to combine the antifungal properties of titanium dioxide, with the adhesive capacity of the copolymer. The synthesis of nanocomposites allows to obtain better properties and performance than the simple mixing of nanoparticles and polymers.

These nanocomposites are useful in many fields, such as antimicrobial coatings for surfaces in cultural heritage conservation, and in particular the antimicrobial protection of substrates based on cellulosic materials was studied. In fact, these materials are subjected to biodeterioration phenomena by biodeteriogenic agents, in particular, fungi.

The choice of starting comonomers for copolymers synthesis was made in accordance with the requirements of low environmental impact and affinity with cellulosic substrates.

Subsequently, it was synthesized an allyl saccharide monomer (allyl α,α'-trehalose) that was copolymerized with vinyl acetate through radical copolymerization reaction (2). Furthermore, the nanocomposites were synthesized with three different molar ratios between the starting monomers and the nanoparticles, to evaluate the different factors and the different growth of copolymers on the nanoparticles.

All the products were characterized by FT-IR and ^{1}H-NMR spectroscopy and TEM microscopy.

Applicative studies were carried out to evaluate the behavior of the nanocomposites in terms of stability of the dispersions, photocatalytic and antimicrobial activities.

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WS5 PO04

Crosslinkers for polyvinyl alcohol-based formulations

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In this work the role of two types of commercial crosslinkers based on polyisocyanate in the variation of the application properties of polyvinyl adhesives was studied. This research was promoted by Vinavil company to obtain information on the different behavior observed in the use of analogous crosslinkers with different formulations of commercial polyvinyl adhesives. In fact, the recent safety regulations have led to research of new formulations based on PVAc with high safety and low environmental impact, maintaining high performance. This research is fundamental in anticipation of a future tightening of the legislation. In particular, formulations without NMA (N-methylolacrylamide) in order to eliminate formaldehyde emissions were studied and appropriate crosslinkers capable of conducting at high performance were selected. The tested commercial crosslinkers (DESMODUR® DA-L and EASAQUA™ WAT-4) are suitable for use with water-based adhesive formulations and showed different behavior with different adhesive formulations, despite the presence in both of hexamethylenediisocyanate trimers. These are differentiated by the strategy with which the molecules have been made similar to the aqueous phase: in DA-L a hydrophilic group is inserted on an isocyanate group, while in WAT-4 free ionic groups are present.

At first, the crosslinkers formulations were studied in presence of water, also studying the gelling capacity of the systems and evaluating the possible use of these systems to produce chemical gels. Moreover, the reactions in the presence of polyvinyl adhesives were studied, evaluating the residual solubility of the components such as PVAc and PVOH, used as colloid protector. With this purpose, the films obtained from the mixing between adhesive and crosslinker were extracted with solvents of different polarity and analyzed by NMR and FT-IR spectroscopy.

In agreement with the literature (1), it has been observed that the presence of NMA with the concomitant presence of $AlCl_3$ is sufficient to obtain low solubility for PVOH but also for PVAc; the use of crosslinkers has not shown any further reductions. Instead, for polyvinyl adhesives lacking one of the two components, the actual role of the crosslinkers in terms of solubility reduction was observed.

From the comparison of these data with the application performances it is possible to highlight the importance of the hydrophobicity of the crosslinker in making the adhesive film more resistant to the penetration of water in the joint. In fact, in the presence of Polymeric diphenylmethane diisocyanate (PMDI) as hydrophobic crosslinkers, the solubility was comparable while performance results were much better. Another fundamental factor is the interaction that is created between the wood and the adhesive formulation.

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WS5 PO05

Methodologies for the sustainability evaluation of novel chemical products for innovative renewable energy technologies

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The design and optimization of novel chemical products and processes for energy generation technologies should be always supported by sustainability assessment (1, 2). This is essential to provide a reliable appraisal of the environmental, economic and social burdens associated to a product or process, and reasonable market implications. Methodologies based on Life Cycle Thinking approach (i.e., Life Cycle Assessment, Life Cycle Costing, Social Life Cycle Assessment, Life Cycle Sustainability Assessment) are strategic tools to achieve this aim.

In particular, Life Cycle Assessment (LCA) is diffusely applied to perform an environmental assessment in this field (3). If used to its fullest potential, it allows a multi-level investigation of the system integrating resource and energy efficiency optimization, critical raw materials analysis and circular economy aspects (4). The LCA analytical approach permits an outlining of the environmental profile of a product or process system during its whole life cycle, from raw materials extraction to end-of-life phase.

In this work, we present the major outcomes resulting from the application of LCA to innovative chemical products for renewable energy production technologies. The analysis is performed for the calculation of the environmental footprint to highlight the hotspots of the system under study, focusing on the behavior of the novel chemical products employed in the investigated energy production technologies. In particular, we investigated the environmental burden and the more sustainable alternatives of some chemical compounds diffusely used in innovative photovoltaic technologies (4).

This poster is also presented as BE PO11

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WS5 PO06

Increasing sustainability of materials for renewable energy

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Why should an industry invest in sustainable products? The first answer is that nowadays polluting have an increasing cost: regulations and taxes on polluting emissions are more and more expensive. The second answer is that finding sustainable alternatives to traditional products give them an advantage when new regulation will be promulgated. It is worth to mention that the public opinion awareness of environmental issues is rising, so the customers who pay attention on the sustainability of a product are increasing.

One of the pillars of sustainable development is the transition from fossil fuels to renewable energies. Hydroelectric, wind, geothermal and solar energies, which are by their very nature renewable, but, nowadays, photovoltaic materials and technologies jeopardize their sustainability.

In particular, considering solar energy, we carried out a study on how the research put its efforts in exploring the sustainability of emerging photovoltaic (PV) technologies with particular attention on organic photovoltaics, dye sensitized solar cells and perovskite solar cells. We observed that the investigations on these emerging PVs are mainly focused on high efficiencies and low costs; anyway, the researches on the environmental impact assessment and the eco-design of these technologies are progressively increasing (1, 2, 3).

Through the identification of the hotspots of these technologies, our purpose is to highlight the trends and the opportunities towards more sustainable alternatives for non-sustainable materials and processes exploited in the production of the final devices.

Through the analysis of life cycle assessments present in literature, we have selected, so far, three common hotspots causing the highest environmental impacts: the coated glass, the precious metals used in the cathode and the significant use of solvents both in the synthesis and in the processing steps of the molecules.

With the aim of increasing the sustainability of emerging PVs, our research work is oriented towards the development of more sustainable materials looking for innovative and alternative sources and processes.

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WS5 PO07

Regeneration tests of a catalytic DPF at the exhaust of a common-rail diesel engine

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The wall flow diesel particulate filter (DPF) is the common soot abatement post-treatment device in Diesel engines, showing the best compromise between a high filtration efficiency and sustainable pressure drop (1). It is characterized by alternatively plugged square channels, to force the exhaust to flow through the porous walls, so blocking the soot (2). Soot accumulation lead to a non-negligible increase of the pressure drop, and the periodic burning of the accumulated soot is mandatory for its regeneration made by after and post fuel injection strategies (1). This work focuses on the comparison of the performance of a bare silicon carbide (SiC) wall flow DPF and of a catalytic one with 30%wt $CuFe_2O_4$ loading. The filters, with a total volume of about 3,5 dm^3, were assembled starting by commercial SiC monoliths (Pirelli Ecotechnology, 150 cpsi), previously treated in order to increase the initial average pore diameter (3). The selected controlled erosion procedure allowed to obtain for the bare monoliths (i) an average diameter increase from 17 to 24 μm and (ii) the increase of the specific surface area from 0.35 m^2/g up to 2.20 m^2/g after 30 minutes of treatment, considered as the optimal time for the pretreatment, and (iii) an increased average pore diameter of the catalytic samples, if compared with the analogues without acid treatment. The experimental tests of soot deposition and DPF regeneration strategy by post injections, were performed at the exhaust of a EURO V light duty Diesel engine available at the engine test bench of University of Salerno (4). The regeneration phase started when the soot load on the filter was about 5 g/l. Both the tested filters showed a very good filtration efficiency, higher than 96% during the whole soot accumulation phase. It is very important to highlight that the results of the regeneration test (figure 1) evidenced that, despite the loose soot/catalyst contact realised, a very good catalytic activity was showed by the catalysed DPF, with a regeneration temperature of about 400°C, sensibly lower than that required by the uncatalytic one (about 530°C) (5). Furthermore, the catalytic DPF allowed positive side effects: i) the NOx and HC-CO emissions reduction, respectively due to the shorter EGR valve closing and to reduced post-injections, (ii) the lower temperature across the catalytic DPF could help in preventing potential thermal failures in the exhaust pipe.

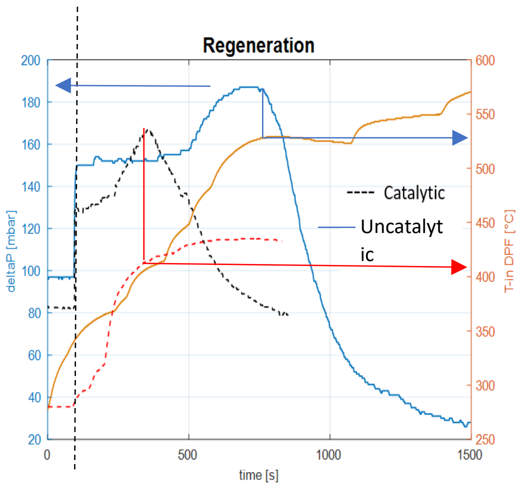

Figure 1. ΔP (dotted black curve) and inlet Temperature (T-in) (dotted red curve) vs regeneration time for 30%wt $CuFe_2O_4$ catalytic filter and the uncatalytic DPF (continuous lines).

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WS5PO08

Carbonylative Regio- and Stereoselective Synthesis of (*Z*)-2-(2-Oxopyrrolidin-3-ylidene)acetates

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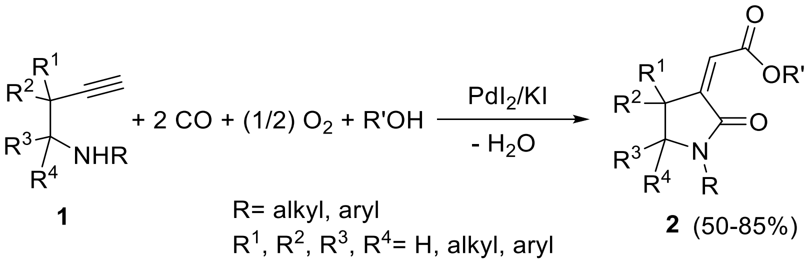
The γ-lactam core is an important structural motif in a large number of biologically active natural productsand synthetic small pharmaceutical molecules for the potential treatment of cancer, cardiac arrhythmia, hypertension and disorders of the central nervous system. (1)

In this contribution, we report a new synthesis of (*Z*)-2-(2-oxopyrrolidin-3-ylidene)acetates **2** by regio- and stereoselective PdI_2-catalyzed oxidative cyclocarbonylation-alkoxycarbonylation of *N*-substituted-3-yn-1-amines **1**, according to Equation 1. The structure of a representative product ($R^1 = R^2 = R^3 = R^4 = H$, $R^5 = Ph$, $R' = Me$) has been confirmed by XRD analysis.



(1)

Reactions are carried out in alcoholic solvents (R'=Me, Et, *i*-Pr, *t*-Bu), under relatively mild conditions (100°C under 40 atm of a 4:1 mixture of CO-air for 2 h) using 2 mol% of PdI_2, in conjunction with 20 mol% of KI, to give **2** in satisfactory good yields (50-85%).

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WS5 PO09

A new [OSSO]-Fe(III) triflate complex as catalyst for the regioselective ring opening of glycidol to monoalkyl glyceryl ethers

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The present work deals with the regioselective preparation of monoalkyl glyceryl ethers (MAGEs) starting from glycidol (2,3-epoxy-1-propanol) through ring opening reaction with alcohols catalysed by a [OSSO]-Fe(III) triflate complex.

MAGEs are a versatile class of chemical compounds with several industrial applications, in particular they are used as the building blocks for the production of additives (for fuels, lubricants, printing inks etc.), detergents, polymers, pharmaceutical and cosmetic products. (1)

Moreover, glycidol is easily obtained from 2-chloro-1,3-propanediol, produced as waste during the Epicerol® process, the bio-based production of epichlorohydrin from glycerol. (2)

As a matter of fact, commercial metal salts such as triflates of Fe(III), Al(III), and Bi(III) were able to catalyse the etherification of glycidol with high activity (turnover frequency until 13400 h^{-1}), good chemoselectivity (90%) toward the formation of twelve monoalkyl glyceryl ethers (MAGEs) but quite low regioselectivity (around 75% of non-symmetric regioisomer). (3,4)

For the first time a well-defined homogeneous Fe(III)-triflate complex, bearing an [OSSO]-type ligand, was reported to catalyse the ring-opening of glycidol with alcohols (Figure 1) under mild reaction conditions (0.05 mol% of catalyst and 80 °C).

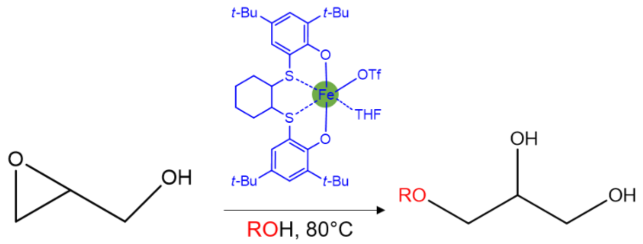

Figure 1. Monoalkyl glyceryl ethers synthesis from glycidol catalysed by Fe(III)-triflate complex.

The reaction proceeds with high activity (initial turnover frequency of 1680 h^{-1} for ethanol), chemoselectivity (>95%) and regioselective (until 96% of non-symmetric regioisomer).

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WS5 PO10

Production of value-added chemicals starting from glycidol as green feedstock

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The present work deals with the preparation of value-added chemicals such as monoalkyl glyceryl ethers (MAGEs) (1), solketal (2) and propylene glycol (3) starting from glycidol.

Recently, we have proposed an innovative synthetic pathway to produce glycidol through a new and highly efficient route based on the conversion of 2-chloro-1,3-propanediol, a by-product in the epichlorohydrin production plant. In this scenario, the use of glycidol as starting material to produce valuable chemicals appears to be very promising. (4)

MAGEs were synthesized under solvent free conditions by ring opening reaction of glycidol with alcohols in the presence of both Lewis and Bronsted acids under homogeneous and heterogeneous conditions at 80°C. Homogeneous catalyst such as $Bi(OTf)_3$ and $Al(OTf)_3$, gave the desired products in only 1 h with a very low catalyst loading of 0.01, high selectivities (>90%) and conversions of glycidol. (5,6) Among of heterogeneous catalysts, Nafion shows the best performances in terms of conversion and selectivity to MAGES and high stability favouring the total conversion of glycidol to MAGEs under mild reaction conditions (80°C, 3h, 0.5% in moles of catalyst). (7)

Solketal was synthesized from glycidol and acetone using heterogeneous catalysts under mild reaction conditions. Nafion NR50, in fact, promotes the quantitative and selective acetalization of glycidol with acetone.

Furthermore, glycidol has been used as starting material in the synthesis of propylene glycol through hydrogenolysis catalysed by Pd/C/Amberlyst-15 in the presence of green solvents.

Finally, in order to evaluate the green potential of the processes, a simplified life cycle approach was followed by comparing the sustainability of the proposed routes from glycidol with that of the most investigated pathway from glycerol.

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WS5 PO11

Kinetics of the Amberlite IR-120 catalyzed acid esterification of ethanol with levulinic acid

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Levulinic acid (LA) is one of the most important platform chemicals as it is a versatile building block for a variety of high value-added agrochemicals, fine chemicals and pharmaceutical intermediates. Catalytic esterification of LA with alkyl alcohols leads to levulinate esters which can be used as fragrances, flavouring agents, as well as fuel additives (1). Ethyl levulinate (EL) can be produced through catalytic esterification of levulinic acid with ethanol. Esterification reactions are usually carried out in liquid phase using mineral acids such as H_2SO_4, H_3PO_4 or HCl as homogeneous catalysts. However, heterogeneous catalysts are preferable because the separation problems associated with homogeneous catalysts are avoided: heterogeneous catalysts are easily recovered and reused. Different catalysts have been already screened for the esterification of LA with ethanol (i.e. ion exchange resins, zeolites, sulfated metal oxides, silica) (1,2). Earlier studies (3,4) have established that the cation exchange resin Amberlite IR 120 as an affordable, green esterification catalyst capable of being used repeatedly without a significant decrease in its capacity.

In the present work, the kinetics of the levulinic acid esterification with ethanol in the presence of Amberlite IR120 was investigated. Experiments were conducted by evaluating the effect of different operating conditions on the reaction rate (i.e. stirring rate, temperature, catalyst loading and reactants ratio). Through this study it was possible to evaluate the activation energy value (3.86 kJ/mol). The collected experimental data were interpreted with a reliable model taking into account also for the mass transfer phenomena involved in the reaction network, such as eventual fluid-solid and intraparticle mass-transfer limitations. The results can be considered as good starting point for continuous reactors optimization.

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WS5 PO12

Bio-based Rigid Polyurethane foams from renewable resources

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Polyurethanes (PU) are one of the most versatile classes of polymers; their structure can be tailored to fit specific requirements by a correct selection of the precursors (1). Most commonly, they are used for flexible and rigid foams, but they also have significant applications in coatings, adhesives, sealants, and elastomers. Typically, the main reagents used to produce polyurethanes (polyol and isocyanate) are derived from oil. However, several concerns about environment and sustainability have triggered a research for bio-renewable feedstocks for the production of these materials.

In this work a bio-precursor obtained by a two steps procedure esterification and polycondensation reactions of some lignocellulosic biomass products (succinic acid and 1,4 butanediol) was, partially, used as OH source, furthermore to increase the environmental aspects in the synthesis of rigid polyurethane foams the remaining polyol used was a commercial bio-based polyol derived from renewable sources (Cardanol from Cardolite). These represent an excellent approach to help to protect and improve the quality of our environment. The thermal, in terms of thermal degradation and thermal conductivity, and mechanical properties were evaluated and compared to a conventional rigid polyurethane foam produced by using water as blowing agent.

The produced foams show a thermal degradation and mechanical behavior similar to the commercial polyurethane, furthermore the thermal insulation property (thermal conductivity) is lower (Foam 2: 0.028 W/mK) with respect to the thermal conductivity of conventional polyurethane (0.032 W/mK).

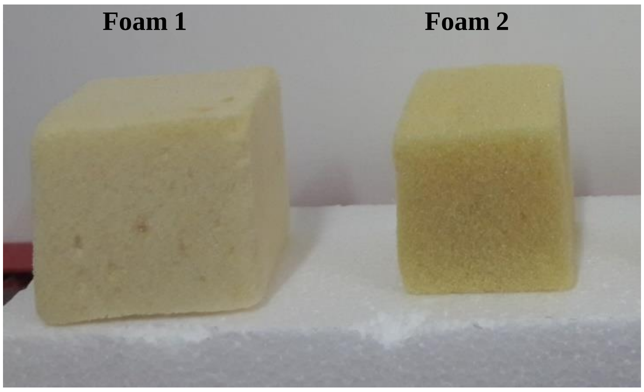

Fig.1: Foams produced starting from different amount of succinic bio-polyol (Foam 1: 50wt% and Foam 2:70wt%) and bio-based polyol from cardanol

With few additional efforts, the bio-based produced foams could be used as thermal insulators in building applications.

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WS5 PO13

Effect of mesoporous zeolites for the selective conversion of carbohydrates into methyl lactate

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The depletion of fossil fuels and the need to find eco-friendly alternative resources has pushed the academic and industrial research to find renewable and more sustainable alternatives for every-day use goods like plastics. A well-known example is given by lactic acid (LA) and its esters (ML) which represent promising bio-building blocks: they derive from renewable biomass like sugarcane and corn and are used for the production of polylactic acid (PLA).

PLA is a biodegradable thermoplastic polyester, it is mainly produced with a solvent-free process in combination with a distillation which involve a first cyclic intermediate (lactide) and its subsequent opening with polymerization. With an industrial production of 206 Ktons (1) per year, PLA finds a wide range of applications ranging from plastic bottles, textiles and food packages.

The production of ML from glucose had already shown great efficiency when using a Sn-beta zeolite as catalyst due to the synergistic effect of Lewis acid sites and crystalline structure (2).

However, the microcrystalline structure present in the zeolite can lead to some limitations when dealing with bulky substrates, inducing to a limited choice of substrate. Considering that biomasses are often a mixture of biopolymers, finding a catalyst able to deal efficiently with complex molecules is convenient both in terms of valorization of the starting material and from an energetic point of view, avoiding different step of preparation of the substrate.

Therefore, different synthetic routes for the formation of mesopores have been performed on BEA and FAU frameworks and tested with inulin and sucrose as model bulky substrates since they are oligomers made up of glucose and fructose units. This allowed the investigation of the effect of mesopores on the reaction pathway and their influence on the formation of products and intermediates.

The full substrate conversion and unaffected yield into methyl lactate confirmed the selectivity of the new synthesized catalysts. A faster formation of the intermediate methyl-fructosides and the product methyl lactate showed that the presence of mesopores aid the entrance of bulky molecules into the active site, due to lower diffusional limitations, speeding up the reaction rate (3).

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WS5 PO14

Production of green polymeric formulations from natural and renewable sources

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The exploitation of renewable materials coming from biomass for the production of green formulations is a strategic objective for the chemical industry in order to reduce the consumption of fossil resources resolving, at the same time, the waste disposal. The sustainability of a process is strongly dependent on the choice of raw materials able to produce high value derivatives or common materials without modifying the availability of natural resources (especially food supply) for the future generations.

In this context, several new biopolymers, bioadditives and nanocomposites were synthesized from "green monomers", obtained using renewable feedstocks potentially achievable from a biorefinery process. The choice of renewable starting materials was made in accordance with the growing interest for the exploitation of lignocellulosic biomasses and the valorization of wastes recovered from food processing and agro-industries.

Different kinds of polyamides with different chemical-physical characteristics according to the choice of monomers were obtained from natural raw materials. In particular, water soluble oligoamides have been synthesized from derivatives of natural substances, that are biocompatible, biodegradable, cheap and with high stability, such as L-tartaric acid, α,α'-trehalose, and L-lysine (1,2). Allyl saccharide monomers were synthesized from α,α'-trehalose or methyl α/β-D-glucopyranoside and copolymers of these allyl monomers were obtained with vinyl acetate through radical copolymerization reactions (3). Allyl α,α'-trehalose/vinyl alcohol and allyl methyl α/β-D-glucopyranoside/vinyl alcohol copolymers were prepared by hydrolysis of the corresponding vinyl acetate copolymers in order to produce water soluble products (3). Properly designed synthetic procedures were used to obtain copolymers with high purity and avoiding protection/deprotection steps in agreement with the principles of green chemistry and industrial sustainability.

The synthesis of biosurfactants and other bioadditives via esterification of products obtainable from biomass was also studied using different reagents as saccharides, ethylene glycol, glycerine, castor oil and oleic acid potentially achievable from a biorefinery.

Finally, several nanocomposites with core-shell structure and potential antimicrobial and antifungal activity were also synthesized using functionalized TiO_2 nanoparticles and applicative studies on cellulosic substrates were performed to test their antifungal properties (4).

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WS5 PO15

Hi-tech cosmetics by cocoa and black tea extracts: a valuable synergy of technologies to transform waste in high value products

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Renewable resources, their use and modification in important industrial processes, have a key influence on our everyday life and are very interesting for an ever-growing cosmetic industry.

The market for new, natural and bioactive ingredients in cosmetics is, in particular, very large and increasing. The use of biomass derived substances can make sustainable products and they can contribute to new, attractive and functional properties. The present work aims to formulate Hi-Tech cosmetic products by using biomass extracts as functional ingredients.

The attention was focused on agri-food wastes and in particular on cocoa bean shells and on by-products of black tea (Ceylon Orange) processing. The green ultrasound assisted extraction protocols used for the biomass treatment (1), produces precious extracts which are rich in antioxidant flavanols (catechins and epicatechins), theobromine, caffeine, gallic acid (whose composition depends on the type of biomass). All these molecules are valuable ingredients for the formulation of anti-age skin products.

The efficiency of these active components was maximized by the use of a Hi-Tech protocol patented (2) by the Ca' Foscari CATMAT team. This technology is based on a sustainable and effective sol-gel approach that assures the optimal dosing, bioavailability and efficacy of functional ingredients by the exploitation of the Drug Delivery Systems technology (DDS, controlled release of an active molecule). A hybrid organic-inorganic network made of polysaccharides, inorganic derivate as silica and acid such as glycolic acids was used as matrix. The formulation was optimized by adding the appropriate rheological modifiers and the appropriate excipient but avoiding the use of surfactants or preservatives. The reagents ratio and the synthetic parameters were optimized in order to adapt the formulation protocol to the biomass extracts with the aim to obtain a final product not only performant but also pleasant for the customers. The use of biomass derived functional ingredients involve, in fact, several critical issues concerning in particular their complexity in term of molecular composition and physical features (color, granulometry, smell). The final products features were analyzed in depth by FT-IR, Raman spectroscopy, by rheological tests and by microscopy analyses. The anti-oxidant activity was evaluated by a free radical (1,1- diphenyl-2-picrylhydrazyl, DPPH) method (3). The evaluation of the drug delivery features of the gels was performed *ex vivo* by using a vertical Franz diffusion cell. The skin permeation was studied by a Tape Stripping Approach (4) by using biologically derived membranes.

The synergy between technology and biomass valorization allows the formulation of a sustainable and high performing product, able to release the active ingredients in a controlled way, guaranteeing at the same time an excellent skin permeation.

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WS5 PO16

Glycerol carbonate as an innovative alkylating agent for phenolics

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Organic carbonates (OCs) are an important class of molecules with a wide range of applications and characterised by both low toxicity and good biodegradability. (1) Because of these reasons their importance as chemical intermediates is continuously increasing. Nowadays, cyclic carbonates are synthesized from the corresponding epoxides and CO_2 by a cycloaddition reaction. (2) On the other hand, the utilisation of glycidol, a toxic and carcinogenic compound, as a starting material for the synthesis of glycerol carbonate (GlyC) is not desirable. For this reason, we have recently proposed the utilisation of catechol carbonate (CC) as an alternative, extremely efficient carbonate source for the selective synthesis of a wide plethora of both cyclic alkylene or symmetric dialkyl carbonates, by the reactions with the parent aliphatic alcohols or polyols. Indeed, starting from a stoichiometric amount of glycerol and CC, in the presence of a basic catalyst (e.g. $NaOCH_3$ or MgO) at very mild reaction conditions (60°C, ambient pressure, 30 minutes) the quantitative, selective, formation of GlyC was achieved with only catechol as the co-product of the reaction. (3) For this reason, the so-formed GlyC was tested as a pioneering alkylating agent for catechol, by only increasing the temperature from the previous step, in a one-pot strategy. Indeed, only few works in literature have investigated the possibility of using GlyC as alkylating agent for the derivatization of aromatic compounds. (4) In this way, 2-hydroxymethyl-1,4-benzodioxane (HMB), has been selectively synthesized, without requiring any reaction solvent nor halogenated compounds, in the presence of both homogeneous ($NaOCH_3$) or heterogeneous (MgO, Na-Mordenite) basic catalysts. HMB is a key intermediate for pharmaceutical industries because its moiety is present in many active principles such as antidepressant (e.g. Doxasozin), antihypertensive and antithrombotic drugs to name a few. Currently, HMB synthesis required a multistep sequence of reactions and the use of toxic solvents (DCM and DMF) and reagents (glycidol derivatives, pyridine etc.). (5) In our optimized conditions, a slight excess of GlyC has been reacted with catechol in the presence of a homogeneous basic catalyst ($NaOCH_3$) at 170°C for just one hour; both reagents have been quantitatively converted with a HMB yield up to 88%. Notably, the main side product, the HMB isomer, may be an interesting intermediate for the synthesis of calone analogues, which are important scaffolds used in fragrances. Moreover, a detailed mechanistic study, supported by kinetics, GC-MS, and HMBC NMR has been performed, underscoring the unique behaviour of GlyC compared to other organic carbonates (e.g. propylene carbonate) and the importance of GlyC as a multifunctional structure, in particular of the free aliphatic -OH group. The latter plays a fundamental role in obtaining the reactive carbonate intermediate responsible for the intramolecular cyclization aimed at the selective formation of HMB, with only water and carbon dioxide as benign coproducts. The reported results represent a completely innovative and greener synthesis pathway to benzodioxanes which was patented. (6,7) Finally, the reaction of glycerol carbonate and phenol has been investigated tuning the reaction conditions with the aim of optimizing the synthesis of mono or di-phenylglyceryl ethers, the latter being elusive with the traditional synthesis using glycidol or epichlorohydrin.

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WS5 PO17

Bio-lubricants Synthesis from the Epoxidized Oil promoted by Clays: Kinetic modelling

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Bio-based lubricants are an attractive class of products, gaining more attention in the recent years. The production of bio-based lubricants starting from vegetable oils derivates (e.g. epoxidized) and alcohols is gaining relevance among the various synthetic routes. Brøensted acids are normally used to promote the oxirane ring opening reaction, obtaining interesting products depending on the branching and chain length of the alcohol molecule. The use of homogeneous catalysts leads to evident drawbacks that could be overcome by replacing them with heterogeneous catalysts. Clays can be considered good candidates as they show reasonable acidity and are characterized by high availability and low price. In the present paper, the use of TONSIL EX 2166 was demonstrated to be very efficient in the synthesis of bio-lubricant bases in the presence of 2-butanol. A kinetic model was proposed to describe the physical and chemical phenomena occurring in the reaction network. The oxirane ring opening reactions promoted by clays shown a peculiar phenomenon: a first fast activity is followed by a zero-order straight line trend respect to the oxirane conversion. In order to describe the experimental evidences, we assumed that two sites are present: site 1 following a deactivation as the reaction proceeds; site 2 showing an activity that is linearly dependent on the catalyst concentration but of zero order with respect to the reactants. An example of the experimental data description is reported in Figure 1.

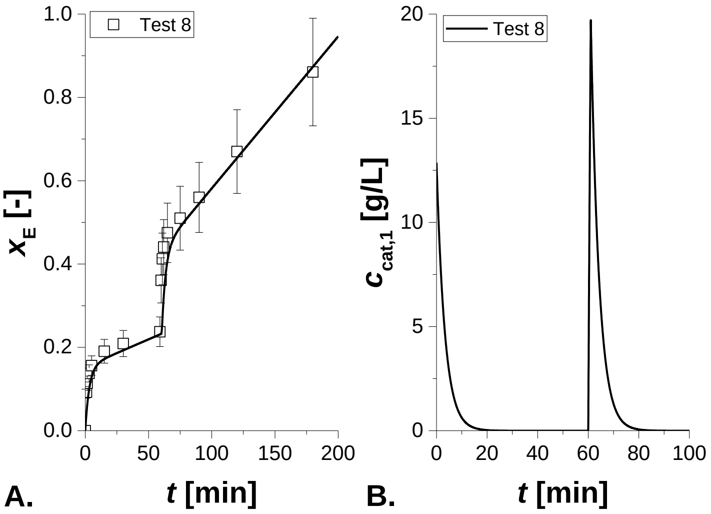

Fig. 1. A. Oxirane conversion trend for an experiment conducted with two additions of fresh catalyst(t=0 and 60min). B. Simulation of site 1 concentration profile.

The model can be considered a starting point for the reactor optimization to scale-up the bio-lubricants production.

WS5 PO18

"GOAST"- Green Organic Agents for Sustainable Tanneries

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Life GOAST project is a European project funded by LIFE Programme, which focuses a novel leather tanning technology. Leather manufacturing is classified as water, energy and waste intensive and it is considered to be an activity demanding for integrated prevention and control of pollution. Nowadays, over 85% of the world leather production is chrome tanned; unfortunately, at certain conditions, and in case of not well controlled process, dangerous chemicals species can be formed, which poses much attention and prompts users to find innovative and more environmentally friendly solutions (1). Therefore, GHOST technology aims to develop a more sustainable tanning process based on the combination of polymer based chemicals and protocol which allows to produce Chrome-Free high-quality leather. This project is an example of synergic collaboration between the university and industrial reality. Indeed, life GOAST project brings together the competencies of an international leader in leather-tanning auxiliary production GSC, with a tannery represented by Conceria Pasubio and waste-water treatment provider Medio Chiampo; the three partners are sustained by UNIVE which gives environmental and technical support to the project.

Thus, life GOAST pays attention to the overall production chain from manufacturing of leather articles to treatment of liquid wastes and solid waste.

Leather solid waste produced by GOAST technology are consequently Cr-free, which can be fully recycled. In view of this, an effective and sustainable process for the valorization of leather waste produced by GOAST technology has been developed.

In particular, the attention has been focused on the enhancement of GOAST shaving waste for the production of "biochar" by pyrolysis and its application as soil improver (2,3). Biochar thanks to its intrinsic characteristic such as: elevated porosity and specific surface, high density, high absorption of organic substances and adsorption of metal cations, can be used as soil improver.

The optimal pyrolysis conditions have been investigated taking into account the effect of different parameters, such as temperature, heating rates, time, grinding size of raw material and inert flow rate, on the characteristics of biochar (4).

The condensable fraction (bio-oil) has been also collected and characterised by GC-MS in order to investigate its chemical composition and figure out its possible industrial applications.

Finally, the thermal degradation of GOAST shaving waste has been studied through the analysis of the evolved gas by thermogravimetric analysis simultaneously coupled with mass spectrometry and Fourier transform infrared spectrometry (TG-IR-FTIR).

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WS5 PO19

Evaluation of *Cynara Cardunculus* Biomass Recovery as an Eco-Sustainable Resource for Bioplastics Bioplasticizers

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Cynara Cardunculus has been attracting an increasing interest in Italy for the bio-plastic industry. Cardoon is a wild robust perennial plant, native from the Mediterranean basin. Its production can reach 30–35 t/(ha year), and the dried flowers of this plant have been used since ancient times in southern Europe as vegetable rennet, to prepare high-quality traditional milk from goat and sheep. Cardoon seeds contain high oil content (25–33%), and their composition is based on mono-, di- and triglycerides. The composition in fatty acids of the Cardoon oil (CO) is similar to that of the soybean oil, around: 60.9% linoleic, 23.6% oleic, 12.1% palmitic and 3.4% stearic acid. Moreover, Cardoon does not compete for land as far as edible resources are concerned, and the related crop does not need high quality of arable land nor fertilisers/herbicide pre-treatment, differently from what happens for materials coming from sunflower or soybean. Cardoon can be cultivated on croplands not competitive with the food chain, such as marginal lands and polluted soils, such as abandoned land previously used for cereal production. Therefore, CO represents an interesting potential non-food plant oil. The aim of this work concerns the study of bioplasticizers for poly(lactic acid) (PLA) to improve the overall properties and broaden its industrial applications as a biodegradable packaging material. Bioplasticizers were prepared by epoxidation reaction of this cost-effective and environmentally friendly oil. Hence, physical blends and films of PLA, containing 3% by weight of CO and ECO, were prepared by melt extrusion and compression molding, and the effect of the both bioplasticizers on structural, thermal, and mechanical properties of the obtained films was investigated. A decrease of glass transition temperature due to PLA was observed, due to a free volume enhancement reduction caused by the presence of oil. This effect was particularly marked in PLA−ECO film. Thermal stability of PLA was meaningfully improved upon addition of the oils, and the mechanical properties made evident the increase of PLA ductility, particularly enhanced in the PLA−ECO system, where the polymeric matrix and the oil showed stronger physical interaction and improved phase compatibility, as also revealed by spectroscopic and morphological analyses. Therefore, the plasticization action exerted by very low concentrations of epoxidized cardoon oil efficiently overcomes PLA drawbacks, thus encouraging the feasibility of its use as a bioplastic for packaging materials.

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WS5 PO20

Sustainable base-lubricant synthesis using heterogeneous catalysts

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Waste raw materials obtained by several sources of both food and agro industries could be considered for biomaterials production. In the last years, this topic has growing in interest, in particular considering the oleins, mixtures of free fatty acids (FFAs) and glycerides. The purpose of this study is related the investigation of the performances of synthetic acid resin (sPSB-SA) as a new heterogeneous catalyst characterized by a high stability at high temperatures (180°C). This catalytic system was tested in esterification reaction in order to obtain biochemical (such as plasticizers or surfactant) and biolubricants (an alternative to the petrochemical lubricants). Typical catalysts used for the esterification reaction are acid homogeneous catalysts such as p-toluen-sulfonic acid, phosphoric acid, sulfuric acid (1). The use of classic heterogeneous catalysts such as acid resins is limited by the fact that they are not stable at temperatures higher than 120°C (1). For the esterification of FFAs, for different applications such as biolubricants synthesis or biochemicals synthesis the temperature must be higher than 180°C to favor the elimination of water from the reaction environment because the reaction is limited by chemical equilibrium. For these reasons the objective of this study has been the investigation of the performances of synthetic acid resin (sPSB-SA) as a heterogeneous catalyst characterized by a high stability at high temperatures (180°C) (2). The catalytic system was tested in a batch reactor and a loop reactor, in order to verify the catalyst stability. The reaction was performed using oleic acid, as references of fatty acid from biomasses (3), and 1,3-propanediol, pentaerythritol, trimethylolpropane as alcohols, in order to obtain different biolubricants bases. The typical reaction conditions were chosen as follows: the temperature was 180°C, the molar ratio (considering the function groups) was 1:1, the catalyst was variable. Acid resin (reticulated and not-reticulated) has shown high activity in esterification reaction and a good resistance to the deactivation. The specific activity of the sPSB-SA resins (referred to the acid equivalent) is similar than that of sulfuric acid conversions of FFA. The introduction of crosslinks in the resin reduces the overall acidity of the resin and consequently its activity but sPSB-SA2 is more stable and it can easily be separated from the reaction products. The results showed that the synthetic resins sPSB-SA1 and sPSB-SA2 (reticulated) had similar activity of sulfuric acid, in particular the resin showed higher activity than all catalysts tested.

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WS5 PO21

Testing hybrid coatings as protective solutions for outdoor lighting systems to be exported to the Middle-East: an effective factory-university collaboration within the TEMART project

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"TEMART" is a project funded by the Veneto Region that raised within a network of companies and universities, in order to develop common strategies for improving manufacturing production through research activity. In particular, the network has two main objectives: it aims at investigating the possibilities given by additive manufacturing and developing innovative technologies to be introduced in the production system. In both cases, proposed solutions must be sustainable reducing materials and energy consuming amounts and limit production costs obtaining objects on macro\micro\nano- scale, made with the most appropriate material (e.g. polymers, metals, composites), innovative in weights and shapes. The application fields considered are design and cultural heritage conservation, with the intent to reach a clientele as large as possible in terms of direct experience of public heritage and availability of design objects on different world-trades. This is the case of lighting systems, thought for outdoor European locations, but now request in the Arabian countries. The issue come upon is the environment: continental in Europe and more critical in the new areas. Chemistry is here asked to improve chemical and mechanical stability of employed components by testing them in different environmental conditions and finding either more performing materials or an accurate way to protect them from sand scraping, effects of higher temperatures and thermal excursion, for example.

The lighting system is made of a stainless steel (AISI 304 steel) body and a polymethyl methacrylate (PMMA) diffusor. Organic and hybrid coatings applied with several methods are being tested, arriving, if possible, to the same solution for preserving both parts of the object. Different coating deposition techniques like physical vapour deposition (PVD-sputtering), atmospheric plasma deposition and sol-gel were tested for realizing silica and hybrid thin films (approximately 1 μm) on both steel and PMMA. A phase for testing adhesion to the substrate and resistance of the different systems is ongoing. Mechanical tests together with chemical analysis will be carried out just after deposition and after accelerated degradation processes with specimens undergoing sudden temperature and relative humidity changes and corrosive attacks (e.g. pH, salt spray), with ageing parameters set on critical environmental conditions. The experimentation has started from already known anticorrosive coatings for copper and aluminium surfaces (1-3) and keeps in mind the ease and sustainability that technological transfer must have at the end. AISI 304 is a steel not intended for outdoor conditions, despite that the coating technology can improve its resistance to external degradation agents, in order to reduce costs production and finding new applications for objects thought for indoor locations mainly. Data collected will be useful for finding the most performing coating system and exporting Italian design on new promising trades.

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WS5 PO22

Innovative material from agro alimentary by-products to realize a spray active packaging in a context of sustainability and Circular Economy

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In the late years, the European Community directives are focusing on an ambitious plan promoting the idea of Circular Economy (1), aimed at waste reduction and enhancing of recycling processes. The main goal of this innovative trend is to move towards environmental sustainability. An interesting example to support the strategy of "closing the loop" is represented by the use of by-products from agro-industrial field that can be inserted in the productive cycles as new resources. High amounts of vegetables are in fact not suitable for commercial use, and large portions of plants are normally discarded. Such by-products are still rich of valuable molecules characterized by bioactive properties, antioxidant and antibacterial (2,3), therefore their use to obtain in new products could provide an additional economic value.

The aim of this study is to use the extracts from this material to realize a new biopolymer characterized by biodegradability and compostability, and that can be used as starting point to obtain an innovative, active and edible packaging.

Experiments to realize the polymer have been made by preparing extracts of by-products derived from onions, artichokes, asparagus, cardoons and grapes, and adding them to selected ingredients, leading to a solution that can be sprayed on food products. The solution, once dried, forms a thin and transparent coating having antioxidant and antibacterial properties, and acts as active packaging that protects the products and enhances their shelf-life. The polymer can be enriched with several active molecules, including flavors, prebiotics and nutraceuticals, tailored for each type of food. The film application has been tested on several products such as meat, fruits and vegetables, and showed a great efficacy in prolonging their shelf-life (4).

Furthermore, this innovative material can represent a good solution to realize several new technologies, according to the new European Directive that banned the single-use plastics by 2021. For example, when sprayed on paper and cellulosic packaging, this product has the effect of realizing a coating impermeable to oils and fats, thus permitting the use of paper to replace multilayer materials based on plastics.

This poster is also presented as BE PO06

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WS5 PO23

The “*virtuous* life-cycle of hydroxyapatite”: from removal of heavy metals in polluted wastewaters to new ecofriendly catalysts for air-quality protection

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In the last decades, the development and improvement of ecofriendly materials for pollution control have been object of intensive research efforts devoted to complying with the ever more stringent legislative constraints for minimizing harmful emission in water and air.

Among all the calcium phosphate materials, calcium hydroxypatite (HAP, $Ca_{10}(PO_4)_6(OH)_2$) is a versatile material that has gained attention in many fields of applied science because of its typical features (e.g. high chemical and thermal stability, extremely low solubility, low cost, large availability and easy synthesis, and ion exchange capability).

Current studies of our research group have proved that this material is able to permanently immobilize polluting hazardous metallic cations (e.g. Cu, Pb, Cr (1)) present in wastewaters with promising yield of removal, if compared with some other adsorbents.

HAP has also found a role in catalysis because of its easy functionalization (2): several metal species of catalytic interest (e.g. Cu, Fe, Mn) can be deposited on its surface with uniform dispersion of metallic centers thanks to the ion exchange ability offered by its structure. The metal obtained HAP samples possess a double functionality, the amphoteric properties, typical of the bare HAP and the electron transfer ability of the metal centers, that are promising properties that can be exploited in catalysis.

Fig. 1: “Virtuous cycle” of HAP

In the view of a more sustainable interaction between environment and industry, we are studying the possibility to employ HAP in a so called “*virtuous* life-cycle” (Fig.1), as sorbent, at first, for removing heavy metals from polluted wastewaters, and then, as metallic catalyst with the possibility to finally recycle both the metallic species and the bare HAP.

In particular, the reuse and valorization of the metal-loaded HAP materials obtained by the first step of de-metallation of wastewaters, allow giving a *second life* to these materials as catalysts in environmental processes for the abatement of harmful gaseous emissions (e.g. de-NOx, de-VOCs, NH_3-SCO, etc.) (3,4).

In this context, the HAP acts as a bridge linking water and air remediation in a fruitful circular process. This is an interesting example of sustainable process and its realization represents an appealing challenge.

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WS6 – MOBILITY

In the frame of CIS2019, the breakthrough-type conference aimed at filling the gap existing between the scientific capabilities of research and the needs of industry and society, a Workshop is organized on the fundamental need of human life: mobility. Main objective of the Workshop is to present, analyze, discuss the contribute of Chemistry to tackle the challenges proposed by Mobility. Main aspects which will be covered are: Sustainability, Smart mobility, Energy for Mobility. Focus will be on vehicles.

WS6 - Organizing Committee and Conveners

- Maurizio Galimberti, Politechnic of Milan, Italy
- Christian Durante, University of Padua, Italy
- Anke Blume, University of Twente, The Netherlands
- Peter Zalar, Holst Centre/TNO, The Netherlands
- Vincenzina Barbera, Polytechnic of Milan, Italy
- Adriano Intiso, SCI Diffusion of Chemical Culture

WS6 - Oral Communications

- **WS6 OR01** – Antonino Salvatore Aricò (ITAE) *"Fuel cells and sustainable hydrogen production for automotive application"*
- **WS6 OR02 -** Raimondo Hippoliti (FIAAM), Matteo Boggian, Stefano Bastianello, Nicola Bortolamei *"Electric Mobility: an overview about the rising transition from Lead Acid to Li-ion battery technology"*
- **WS6 OR03** – Attilio Citterio (Politecnico Milano) *"Chemistry and Materials for sustainable mobility: strategy and perspectives"*
- **WS6 OR04** – Fabian Grunert (University of Twente), Andries van Swaaij, Anke Blume *"How to meet the future mobility requirements of the automotive industry?"*
- **WS6 OR05** – Thomas Hanell (Pirelli) *"Material trends for the tire of the future"*
- **WS6 OR06** – C. Yamada, M. Sato, Amnuwa Beraheng, Kannika Sahakaro, Wilma K. Dierkes, Jacques W.M. Noordermeer, Anke Blume (University of Twente) *"New approaches to reduce the CO2 emission of a passenger car by introducing innovative materials"*
- **WS6 OR07** – Marika Falciano (FCA) *"New materials for future mobility: the automotive sector involvement"*
- **WS6 OR08** – Gianluca Casagrande (Dow), Sabrina Fregni (Dow) *"Innovative polyurethane foams solutions to improve engine efficiency and total weight reduction while enhancing vehicle driver's comfort and safety"*
- **WS6 OR09** – Ulrich Giese (DIK) *"Improvement of tire materials concerning light weight, permeability and rolling resistance using high effective filler systems"*
- **WS6 OR10** – Michele Grazzi (LyondellBasell) *"Advanced Product Performance to meet Light Weight Requirement for Transportation Segment"*
- **WS6 OR11** – Gianpiero Mastinu (Politecnico Milano), Giorgio Previati, Vincenzina Barbera, Maurizio Galimberti "Light weight materials for sustainable mobility: nanofillers and design
- **WS6 OR12** – Gianluca Casagrande (Dow), Sabrina Fregni *"Cabin air quality improvement by low emission, aldehyde abatement and enhanced durability of new generation Polyurethane Interior Foams"*
- **WS6 OR13** – Franco Fattorini (EPTANova), Paolo Giaccone *"Printing and painting industries: processes and products for sustainable mobility"*
- **WS6 OR14** – Mario Caironi (IIT) *"Printed Organic Electronics Solutions for Smart Electronic Systems"*
- **WS6 OR15** – Miguel Ribeiro (CeNTI), N. Durães, S. Silva, D. Esteves, J. Gomes *"Development of nano and micro structured smart fibre devices"*
- **WS6 OR16** – Peter Zalar (Holst Centre / TNO) *"Applied Conformable Printable Sensor Systems"*

WS6 OR01

Fuel cells and sustainable hydrogen production for automotive applications

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Technological improvements in polymer electrolyte membrane fuel cells (PEMFCs) and water electrolysers (PEMWEs) are promoted by their exciting possibilities to support sustainable mobility and operate with renewable power sources while using hydrogen as energy vector. In this communication, a synopsis of the research efforts concerning with the development of electrocatalysts, polymer electrolytes and stack hardware components for fuel cells and electrolysis technologies is presented. One of the main challenges of polymer electrolyte membrane fuel cells (PEMFCs) for automotive applications is represented by the need to operate at medium or high temperatures (above 120 ˚C). In contrast to an internal combustion engine (ICE), which rejects almost half of the heat through the exhaust, a fuel cell has to reject most of the heat through the radiator. Since most of the standard perfluorosulfonic acid based membranes are characterized by a limiting operating temperature of 90 ˚C, additional cooling efforts are necessary to keep the operating temperature at a reasonable temperature level. This aspect implies as large size radiator often not compatible with the required compactness of the car as well as an increase of the system complexity and total cost. Increasing the operating temperature up to ~110-130 ˚C would alleviate this drawback and improve the catalyst behaviour. As an example, high temperature operation will reduce the size of the thermal subsystem, improve reaction kinetics and increase tolerance to impurities contained in the reactant stream, e.g. CO possibly contained in the hydrogen stream. Moreover, there is the need to reduce the precious metal content in the fuel cells stack to favour large-scale deployment of this technology.

The most challenging problem for the development of PEMWEs is the enhancement of oxygen evolution reaction rate. At present, there are no practical alternatives to noble metal-based oxide catalysts such as IrO_2 and RuO_2. As well as carbon supported Pt nanoparticles are the benchmark cathode catalysts for hydrogen evolution. High noble metal loading on the electrodes and the use of perfluorosulfonic membranes significantly contribute to the cost of these devices. Critical areas include the design of appropriate mixed electrocatalysts and their dispersion on low cost Ti-oxide like supports to increase catalyst utilization. Moreover, the development of alternative membranes with enhanced mechanical properties for high pressure applications, proper conductivity and reduced gas cross-over is strongly required. This latter aspect is also addressed by the development of proper recombination catalysts. Concerning with stack hardware, cost reduction may be addressed by replacing Ti-based diffusion media and bipolar plates with appropriate and cost-effective coated stainless steel materials with enhanced resilience to chemical and electrochemical corrosion. Regarding the combination with renewable power sources, PEM electrolysers can find suitable applications for peak shaving in integrated systems grid connected or in grid independent operating conditions where hydrogen generated through electrolysis is stored and then via fuel cell converted back to electricity when needed or used to refill fuel cell-based cars. Hydrogen is the most promising clean energy carrier to accomplish the sustainable production of energy and a synergy among hydrogen, electricity and renewable energy sources is highly desired.

WS6 OR02

Electric Mobility: an overview about the rising transition from Lead Acid to Li-ion battery technology

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Nowadays mobility electrification is gaining more and more interest due to increasingly stringent regulations on vehicles CO_2 emissions. The architecture of vehicles powertrain is heavily under redefinition and consequently the electric energy source as well. With regard to batteries, carmakers and battery suppliers are going to be forced to leave Lead-acid battery technology in favor of more performing and eco-sustainable solutions, as lead based batteries suffer of some performances limitations (e.g. limited energy recovery capability, energy and power density) and may undergo to a legislative restriction due to the potential future Lead ban.

Therefore, there is a need to implement alternative technologies, maintaining the current safety levels, while increasing the energy and power throughput at recoverable costs.

During this talk, the current and future technological and market scenario is presented based on our joint projects with Hitachi Chemical and on the regular meetings with automotive OEMs and European committees.

Lithium-ion batteries technology appears as the most promising solution to replace Lead-acid technology in terms of performances and technology maturity.

The chemistry of the cells strongly influences the Lithium-ion battery performances and costs. The main driver at this regard is the cathode material and its availability, so that current adopted chemistries are NMC622, LFP and NCA, whereas NMC811 is assumed as the most promising for the next future. Besides the cell chemistry definition, carmakers and batteries suppliers are developing different architectures based on short, medium and long term solutions.

The short-term solution is to replace the traditional 12V Lead-acid battery with a 12V Lithium-ion battery overcoming the potential Lead ban and the payment of high fines for emissions. At the moment, the most challenging issue faced by carmakers and batteries suppliers is the cranking performance at -30°C. Actual cells chemistries are not able to guarantee at the same time the requested cranking performances at low temperature and cost competitiveness. In order to avoid this issue, a multi-chemistry battery can be assembled. This battery is composed by cells strings of different chemistries and – sometimes in addition – by a string of a supercapacitors as well.

The medium-term solution is to hybridize the vehicle powertrain assisting the propulsion of the internal combustion engine (ICE) with electric motors (EMs) in order to reduce fuel consumption and consequently CO_2 emissions. The hybridization level of a powertrain depends on the Lithium-ion battery voltage and energy. The 48V Mild-Hybrid architecture is the solution with the lowest impact on the vehicle structure and cost, while reducing CO_2 emissions. This solution is also very attractive for the market thanks to the possibility to introduce advanced driver assistance systems (ADAS) in the vehicle which require a certain amount of energy.

The long-term solution consists in increasing the Lithium-ion battery pack voltage turning the hybridization level from a full-hybrid architecture (about 300V) – that allows to drive in electric mode for a very limited amount of kilometers – to a full-electric architecture (about 600V). These solutions require an high integration level between vehicle and battery pack and an accurate management of isolation due to the high voltage.

The aforementioned transitions are rising in all the mobility applications, from passenger to commercial/public vehicles; an extended implementation in series vehicles will strongly depends on the political and regulatory environment and will require a strong effort in the technological development, investments and infrastructures.

WS6 OR03

Chemistry and Materials for sustainable mobility: strategy and perspectives

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Sustainability in the field of chemistry and materials moves from the appropriate selection of sources. 200 gigatons of biomass are available per year and only 4% are used by humans. The European Parliament, already in 2013, made clear which natural sources should be taken into consideration: stated that "The recent experience of the development of certain renewable energy sources, particularly biofuels from food and feed crops such as cereals, oilseeds and sugar, has stimulated concern that new biorefinery processes must as far as possible be based on non-competing wastes and residues to minimise impacts on food availability and prices." Two major areas of development can be envisaged for biomass: (i) for energy uses, directly or after conversion (ii) as base source for chemicals, materials and products

Great attention should be for wastes and residues: "some of these materials have largely been considered a nuisance, and a challenge for disposal without polluting the environment. It is highly attractive therefore to be able to switch mind-set and see such materials as useful feedstocks or raw materials."

A fundamental role is then played by the strategy for R&D. One could develop a sort of biomimetic strategy also for materials made by human beings: nature is indeed sustainable. Or would it better to develop an alternative and innovative pathway?

This contribution discusses these themes, focusing the attention on chemistry and materials used in view of basic needs of the mobility sector.

WS6 OR04

How to meet the future mobility requirements of the automotive industry?

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The automotive industry is one of the main driving forces for the European economy, provides employment to 12 million workers. But the sector is facing many structural changes, including stricter emission standards and decarbonisation as part of new mobility concepts. A high quality of education, skills and training is the basis to ensure the strong position of the automotive industry in the future: knowledge, innovation, R&D and competence development are mainly important. The future jobs will have a different mix of skills and requires permanent upgrading of skill levels and competences. The European DRIVES project is dealing with this challenge.

WS6 OR05

The Challenges of Sustainable Development in Tyre Materials

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Tyres integrate hundreds of raw materials and diverse technologies: tyres are then complex engineered products.

Tyre development is driven by the requests of vehicle manufacturers, legislation and market forces: Pirelli integrates the former inputs into an Open Innovation Model, involving collaborations with OE customers, selected suppliers and research institutes. Pirelli's R&D effort is based on Key Enabling Technologies: Micro-Nano Electronics, Nanotechnology, Industrial Biotechnology, Advanced Materials, Advanced Manufacturing Systems.

Pirelli is strongly committed to the development of high performance products and to their continuous improvement in terms of safety and environmental impact, according to its "green performance" strategy "safe for People, safe for the Planet".

Pirelli set in 2018 ambitious objectives on product and raw materials:

- Product: to improve noise by 15%, rolling resistance by 20%, and wet grip by 15% within 2020 (reference 2009 values)
- Raw materials: for selected segments Pirelli will double the share of renewable materials and reduce the fossil based materials by 30% within 2025 vs 2017

New Materials and Technologies are a fundamental part of Pirelli's Innovation Strategy. Main developments in new materials are:

i) New Polymers to resolve trade-offs between Rolling Resistance, Wet and Winter performances

ii) Chemicals from renewable feedstock with potential use as plasticisers, protective and curing agents

iii) Nanofillers and biofillers to support lighter structures and further contribute to reduce the environmental impact of tyres. Nanotechnology plays a key role in Material's Innovation: tyre behaviour depends on compounds' properties from macroscale down to the nanoscale: a big effort is devoted to the understanding and the tailoring of Nanofillers and of their interface with polymers, resulting in the development of new Nano-composites from renewable feedstocks (e.g. lignin and cellulose) and low footprint minerals.

The Development of new Nanocomposites is based on Safe-by-Design strategy.

WS6 OR06

New approaches to reduce the CO_2 emission of a passenger car by introducing innovative materials

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Different approaches exist to reduce the rolling resistance of a passenger car to save CO_2. Due to the fact that the rolling resistance of the tires delivers a significant contribution to the overall rolling resistance of the car, the tire design plays an important role. The tire tread design determines mainly this contribution from the whole tire. Three approaches are presented to reduce the rolling resistance of a passenger car by improving the tire tread design: the idea to functionalize the polymers used inside the tire tread, the introduction of an alternative coupling agent to combine the polymer with the filler and the introduction of a bio-based oil as a replacement of the traditional used oil.

One of the major developments in the tire industry of the last decennia is the introduction of silica to replace carbon black in the tire tread for a reduction of the rolling resistance. However, due to its high degree of filler-filler interaction, it is difficult to disperse silica within the polymer matrix of the tire tread compound. Using a silane coupling agent is the common method to solve this problem. However, this technology poses problems in terms of processing. An alternative promising approach is the functionalization of the elastomer matrix for improving the dispersibility of silica by enhanced silica-polymer interactions. For instance, amine, carboxy and silane groups are well known for functionalizing S-SBR polymer with the aim to improve the dispersion and to reduce the rolling resistance.

Another possibility to improve this existing system is the introduction of a new silane. The use of mercaptosilanes leads to a significant improvement of the rolling resistance. An intensive study was carried out to understand the coupling mechanism to overcome the processing issues.

A further approach to improve the rolling resistance of tires is the replacement of the traditional used distillated treated aromatic oil by an epoxidized bio-oil. The use of epoxidized palm oil leads to an improvement in the rolling resistance without any significant deterioration in further important in-rubber properties.

WS6 OR07

New materials for future mobility: the automotive sector involvement

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The automotive sector is at the center of everyday life. It is in continuous evolution in order to satisfy the new global laws and the new market requirements. The OEM face new challenges regarding the CO_2 emission and reduction, the global warming problem, the limited resources problems and the greatest customers' requests. For these reasons, the automotive sector moves to the design of sustainable vehicles.

Automotive sustainability implies the development of new car concept architecture and systems but also through adoption of new materials leading to a beneficial environmental impact. The future challenges demand the development of a new generation of materials and components and a deeper systemic approach to the vehicle development. These materials have to satisfy the performances, the reliability, the safety and the weight requirements; but, at the same time, they should be eco-friendly. The OEM and the suppliers work together in order to develop these new materials and to exploit their potentials. In particular, FCA is actively committed to several national and European project that focus their attention on the possibility to use lightweight (new fabric structures, hollow fibers textiles, etc.), green (recycled materials, Bio-based polymers, etc.) and multifunctional materials (new aesthetic features, electrically conductive fabrics, integrated electronics for sensors, etc.).

WS6 OR08

Innovative polyurethane foams solutions to improve engine efficiency and total weight reduction while enhancing vehicle driver's comfort and safety

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There are many sources of noise into passengers car vehicles, which can affect the driver's comfort and safety, as well the same vehicles are contributing to the road traffic noise which is a global growing concern: tires and air frictions generate noise which adds to the one from the engine compartment. In 2013, new legislation (No 1386/2013/EU) was established in Europe requiring further reduction of noise levels, which are aimed to be adopted globally. Additionally, the reduced car CO2 emission targets led to new power train developments and technologies to improve fuel efficiency, but at the same time are increasing noise emissions. Therefore, the automotive industry has continuous challenges in further reduce vehicles noise by introducing sound insulating materials and components as well as lightweight to improve fuel consumption. Sound insulation materials are moving away from felt and fiber reinforced materials to lightweight polyurethane (PU) foams because of the better combination of weight saving, acoustic comfort, enhanced durability and fire resistance properties. Furthermore, a new important automotive mega trend is represented by Hybrid/Electrical Vehicles (EV) and compact cars: Asia is a big market for hybrid /EV, while the share of compact cars is globally increased significantly. Therefore, the trend thinning seats is further stressed because of the need to provide extra space to put batteries under rear cushions for hybrid/EV vehicles. Reduced seats weights as well reduced seat thickness and size also improves head and knees space, thus increasing, safety, comfort and the perception of quality & appeal by making interiors look modern.

WS6 OR09

Improvement of tire materials concerning light weight, permeability and rolling resistance using high effective filler systems

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From technical and from sustainability aspects modern tire compounds have to fulfill different properties on very high levels. Concerning innerliner materials low permeation rates are de-sired without any loss of strength and with light weight. Aspired properties to tread compounds are low abrasion and an optimum in traction and rolling resistance. Such high sophisticated properties can be reached using anisotropic fillers like layered silicates, nano-fibrilated cellu-lose (NFC), carbo nano tubes (CNT) or graphene platelets. The high potential of such filler materials can be used only in combination with optimized mixing strategies for high disper-sion. Platelet materials like layered silicates or graphene platelets were incorporated in rubber matrices using a promising special latex mixing technology. Butyl rubber, made from cationic polymerization processes, is well known for low permeation properties. To use the high effec-tive latex mixing technology the preparation of a secondary latex was necessary first. NFC-composites with low density at high mechanical strength and hardness could be prepared. To optimize tread properties, the filler loading could be reduced by high effective CNTs, partially in combination with traditional fillers like Carbon black or silica. Overall the filler raw materials are characterized for their surface properties by means of static gas adsorption. The filler-polymer interaction as an important factor to evaluate the filler performance is characterized using swelling experiments and Kraus-Plot. Furthermore, the permeation and mechanical-dynamical properties as well the reinforcement were investigated.

WS6 OR10

Advanced Product Performance to meet Light Weight Requirement for Transportation Segment

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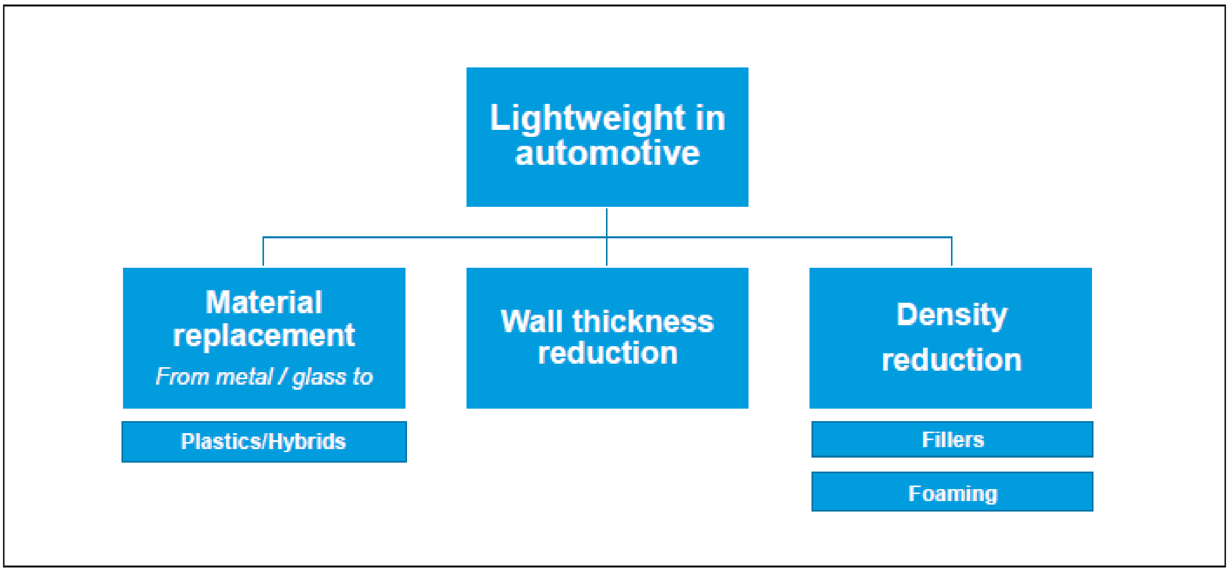
Since years, the Automotive Industry has been receiving from Governments and public opinions a lot of pressure to reduce Greenhouse Gas Emission (GHG) and consequently, many developments activities are nowadays focused on fuel efficiency, durable and lightweight vehicles.

In this framework, with their unique combination of properties, plastics (and polypropylene mainly) are very attractive materials allowing technological innovation and design freedom. Plastics have penetrated automobile parts such as bumpers, fenders, doors, safety and rear-quartet windows, headlight housing, side-view mirrors, trunk lids, hoods, grilles and wheel covers….

In such a context, LyondellBasell is by far worldwide leader in the production of PP based compounds for the Automotive industry as well as n.1 in PP resins production and commercialization.

Lightweight in Automotive can be realized in several ways as it is summarized in the below scheme and Polypropylene developers can address those main factors influencing the weight reduction with innovative product design.



This presentation summarizes recent LyondellBasell's Polypropylene resin developments that serve the manufacturing of PP compounds and will be focused on novel structures enable to fulfill the latest requirements for aesthetic, light and easy-processable materials that can be adapted to meet challenging needs in a cost-effective way while having the lowest environmental impact. Examples of inter-plastics replacement (Polyamide to Polypropylene), density reductions through filler diminution and/or elimination and Polypropylene foamable solutions will be provided.

Presentation will also include solutions developed to comply with the target to reduce the amount of Volatile Organic Compounds (VOC) in resins used by Automotive players in view of the more and more stringent limits set for the qualification of new plastics compounds to be used in their new productions.

WS6 OR11

Importance of anisotropic effects and master curves for rubbers with sp2 carbon allotropes for tyre tread lightweight materials

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This work presents both the basic paradigms on which selecting proper materials for manufacturing tyre tread and the consequent preparation of lightweight rubber materials with nanosized sp2 carbon allotropes. Anisotropic nonlinear mechanical behavior of composites based on these nanofillers are discussed and proposed for application.

Referring to the basic paradigm, we show that the Noise-Vibration-Harshness (NVH) performance of a pneumatic wheel needs lightweight materials to avoid poor performance. We also envisage that an anisotropic behaviour could be beneficial to cope with vertical NVH performance and lateral handling performance. Thus a new lightweight material is presented with the requested anisotropic behaviour.

Referring to lightweight materials, composites were prepared with either poly(styrene-co-butadiene) or poly(1,4-cis-isoprene) as the polymer matrix and either carbon black (CB) or carbon nanotubes (CNT) or hybrid CB/CNT as the filler systems. The initial modulus of the composite (G’□min) was determined through dynamic mechanical shear tests and was correlated with the specific interfacial area (i.a.), calculated through the product of filler surface area, density and volume fraction. Common correlation was established, the equation of the common interpolating curve was derived and was used to design composites with the same modulus and lower density, substituting part of CB with lower amount of the carbon allotrope with larger surface area, CNT. Anisotropic nonlinear mechanical behavior was found for nanocomposites based on CNT and poly(1,4-cis-isoprene), prepared by melt blending, calendering and compression molding. An orthotropic and transversally isotropic response was observed: dynamic-mechanical moduli were very similar inside the sheet plane and very different from those in the orthogonal direction.

The paper shows the benefits that the new materials could provide in terms of NVH and handling performace of a car fitted with tyres with anisotropic rubber.

Cabin air quality improvement by low emission, aldehyde abatement and enhanced durability of new generation Polyurethane Interior Foams

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Cabin air quality is a growing concern raised by the various Original Equipment Manufacturers (OEM) throughout the world. Although a number of countries have established regulations or guidelines regarding acceptable chemical concentrations in automobiles, it is the automotive industry itself that has been the principle force for implementing chemical emissions test methods and requirements for automotive components. Chemical emission testing and reporting is now an essential components procurement requirement for most OEM, and very severe requirements for low Odour, Volatile Organic Compounds (VOC) and aldehyde emissions have been and are continuing to be set by all OEMs. The large variety of test methods consists in accelerated heat aging of the sample in order to understand the potential exposure overtime. Dow Automotive Polyurethane Systems did address and is addressing the need of very low emission PU foams for interiors applications by global development projects as well as investments with respect of emission tests capabilities in Dow laboratories (i.e.: VDA 278, VDA 276, 1 m3 chamber , micro chamber and TEDLAR bag tests). New polymer building blocks as well as the use of specific AntiOxidant package allowed to reduce VOC emission contributions such as Glyco-ethers, Acetaldehydes, Propionaldehydes and Amine antioxidants. The combinations of Low emission PU components with SPECFLEX™ Activ Polyol Additive and non-fugitive catalysts resulted in the development of Specflex fully formulated PU systems for seating, headrest, Instrument Panels and Interior Trims (IPIT) and Noise, Vibration, and Harshness (NVH) applications able to fulfill VOC specifications requirements, without compromising processing, physical mechanical properties and properties retention after humid aging. In addition, Dow is focusing on GEN II low emission technology, targeting even more severe Acetaldehydes and odor reduction requirements: the approach is based on the combinations of Low emission components and differentiated additives that scavenge-up aldehydes produced during the polymerization reaction.

WS6 OR13

Printing and painting industries: processes and products for sustainable mobility

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The contribution to sustainability provided by processes and products in the mobility industries can be remarkable and can operate in various directions, like reduction of emissions and lower energy consumption in the manufacturing processes, longer term performances of structural materials, environmental compliance of utilized coatings and inks and even reduction of fuel consumptions. Future developments may involve fascinating scenarios, thanks to revolutionary applications of high-tech specialties. Eptanova group and parent companies offer an integrated range of products covering industrial printing and digital inks, paints, specialties and related equipments inks, and operate in order to support sustainability approaches in various areas. The basic level of sustainability concepts in mobility is already implemented by most producers of paints for mobility items: removal of high concern materials, progressive switch to low emission technologies is a must in Europe and is growing rapidly in the rest of the world: waterborne coatings are enforced by the laws, UV inks and clear varnishes without thinners, powder coatings where possible, high solid coatings up to 80% are a must in the ACE market, schemes aiming at the reduction of the number of layers. Processwise, important steps are in progress: in the automotive industry lower baking temperatures and faster processes with wet-on-wet schemes, and systems to reduce paint consumption (including primer-finish in a single material) and overspray are being used, like electrostatic applications and more recently strongly innovative application of processes in nitrogen atmosphere,. Furthermore, the use of non-toxic, hull protection silicone-based products for ships ensures respect for the marine fauna and lower fuel consumption thanks to lower friction coefficient. One of the most innovative applications supported by Eptanova ensure safer operating conditions for the car drivers: a new tecnology make sure the driver operates with the better illumination, while conductive inks make possible to monitor physical conditions of the driver, ensuring more safety and accidents prevention.

Printed Organic Electronics Solutions for Smart Electronic Systems

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Printed organic electronics has been considered for many novel applications towards large area and flexible electronics, since it can enable pervasive integration of electronic functionalities in all sorts of appliances, their portability and even wearability.

In this contribution, I will first give an introduction to the basics of printing of functional inks, focusing on the methods and materials. I will then describe recent developments in printed smart systems, including sensors (in particular light detectors and biosensors), power (with focus on light and heat harvesting), and logic (with focus on printed microelectronic circuits). A key role is played by the electronic properties of conjugated polymer semiconductors, and I will in particular show how they can serve different scopes in printed electronics, and show current challenges in their development towards efficient devices suitable for market products.

WS6 OR15

Development of nano and micro structured smart fibre devices

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The integration of Smart functionalities into textiles has been growing in recent years with already some commercial examples in the market, mainly for wearable applications. Even though the increased interest in this research field, the integration of electronic components, such as sensors, batteries or displays into textiles has several limitations regarding the wearability, and the comfort provided by the textiles. On way of overcoming this limitation is the development and integration of fibre-based devices that, due to the similarities to the textile fibres, are less intrusive to the users.

Development of new electroactive materials and their integration into and onto textile structures for sensing and energy harvesting applications has been a common topic of research for the past decade, mainly by direct integration (or encapsulation) of sensing devices onto textile substrates of garments and other textile products. One of the new research trends for the integration of sensor-actuator systems onto/into textile applications is the development of fiber-based (or fiber structured) devices, using fiber or yarn processing methods to obtain the typical multilayer of these devices. Several technologies are commonly used to develop these fibers and yarn based devices, using bi and tri component extrusion and processing electrically active layers directly from melt spinning processes of conductor and semiconductor polymers, yarn and fiber combination via twisting processes, or yarn and fiber coating processes.

In this work, we present the efforts to develop interactive/electroactive fiber and yarn-based structures. The aim is to incorporate sensing and actuation properties directly onto the fiber and yarn structures by processing piezoelectric fibers and yarns to replace conventional bulk electronic devices. Our developments were focused on the study of fiber processing parameters of bi- and tri-component melt spinning technology using electroactive polymers coaxially combined with conductive polymeric compounds in the fiber cross-section. The microstructure and crystalline structure of the processed polymers was studied as function of the processing conditions. Being the polarization of piezoelectric fibers, one of the main challenges, different polarizations approaches were followed focused on a continuous system in line with the textiles and spinning process.

WS6 OR17

Applied Conformable Printable Sensor Systems

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Holst Centre is an Open Innovation research center founded by TNO and IMEC and is located on the High-Tech Campus in Eindhoven, The Netherlands. One of its research areas is “flexible electronics”; targeting devices such as organic lighting emitting diodes (OLEDs), flexible active matrix AM-OLED displays, in-mold electronics, organic photovoltaics (OPVs), flexible sensors, and electronic circuits on flexible substrates.

Interest in flexible and stretchable printed electronic devices has increased due to the demand for the simultaneous combination of conformability, ruggedness, and light weight that traditional electronics simply cannot deliver. Many applications, such as those in the realm of medicine, automotive, or robotics, require conformable sensor systems. This class of electronic devices have the potential to greatly improve the quality of data collected by them while being less obtrusive. To achieve this goal, the development of printable and stretchable sensors along towards reliability and processability is critical. In this presentation, Holst Centre’s recent progress towards sensor systems for applications such as battery management systems will be discussed.

WS6 - Poster Communications

- **WS6 PO01 –** Valerio Margiotta, Maria Cecilia Palumbi, Giancarlo Cossu, Paolo Straffi, Angela Agostiano, M. Lucia Curri, Roberto Comparelli (IPCF-CNR) “*New multifunctional cross-linking promoters in curing process for tyre applications”*
- **WS6 PO02 –** Marika Falciano Vito Guido Lambertini, Paolo Chiappero, Marco Zanetti, Valentina Brunella (FCA) “*Eco-sustainable elastomeric materials for the automotive sector”*
- **WS6 PO03 –** Gea Prioglio, Silvia Agnelli, Winoj Balasooriya, Bernd Schrittesser, Lucia Conzatti, Daniele Locatelli, Vincenzina Barbera, Maurizio Galimberti (Politecnico Milano) “*Sustainable materials for tyres. 1. Natural rubber compounds with better mechanical properties thanks to functionalized nanosized graphite”*
- **WS6 PO04 –** Daniele Locatelli Valeria Cipolletti, Giulia Peli, Luca Giannini, Vincenzina Barbera, Maurizio Galimberti (Politecnico Milano) “*Sustainable materials for tyres. 2. High aspect ratio natural fillers for rubber compounds with low dissipation of energy”*
- **WS6 PO05 –** Fatima Margani, Vincenzina Barbera, Daniele Locatelli, Valeria Cipolletti, Maurizio Galimberti (Politecnico Milano) “*Sustainable materials for tyres. 3. Biobased secondary accelerators for silica based compounds”*
- **WS6 PO06 –** Lucia Rubino, Martina Magrograssi, Vincenzina Barbera, Maurizio Galimberti (Politecnico Milano) “*Sustainable isocyanate-free polyurethanes”*

WS6 PO01

New multifunctional cross-linking promoters in curing process for tyre applications

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Zinc oxide is an extensively used compound in rubber chemistry due to its efficiency in activating on the most important process in tyre industry: vulcanization. Despite the beneficial role of zinc, there are questions regarding the impact of heavy metals on human health and ecological systems when they are released into the environment. These environmental concerns have led to discussion regarding potential governmental regulation of heavy metal compounds in rubber articles and prompted many manufacturers to evaluate strategies to reduce the amount of zinc in formulations. (Nano)materials that possess both crosslinking efficiency and the ability to work as reinforcing fillers could stand as an innovative and profitable application of nanomaterials in rubber chemistry. In the quest to reduce the amount of zinc in rubber, they also represent excellent candidates considered their high surface area.

Herein we report a facile two-step synthesis of zinc phosphate and zinc silicate decorated silica nanoparticles in which tiny zinc-containing "dots" randomly cover the surface of silica nanospheres.(1) In the first step, we synthesized silica nanoparticles with the Stober method, which were subsequently used as seeds to accommodate the heterogeneous nucleation of small nanoparticles based on zinc phosphate and zinc silicate at temperatures as low as 50 °C. As observed by means of Transmission Electron Microscopy, the nanoparticles are well dispersed on the filler particles and leave largely exposed silica surface. Model Compound Vulcanization studies allow to compare the efficiency of $Zn_3(PO_4)_2/SiO_2$ and Zn_2SiO_4/SiO_2 NPs with conventional ZnO. The results show that zinc phosphate and zinc silicate decorated silica nanoparticles possess equal crosslinking efficiency or, in some cases, superior than conventional ZnO when used at the same concentration in terms of zinc ions.

The effect of the novel activators on the vulcanization of isoprene rubber (IR), particularly on the formation rate of the sulfurating complexes at the beginning of reaction and of the sulphur cross-links in the final cured material, has been also investigated.

Nanosized zinc silicate demonstrated better curing efficiency and improved dynamic mechanical properties in cured silica/rubber nanocomposites, when used at 3 phr, compared to those obtained by using the same amount of microcrystalline ZnO. These results suggest the proposed material could be considered as a promising system for the improvement of the curing efficacy and for the effective decrease of Zn^{2+} utilization in rubber compounding.

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WS6 PO02

Eco-sustainable elastomeric materials for the automotive sector

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A smart and sustainable society is also created thanks to the changes in the automotive sector. For this reason, the automotive sector has started to review the car design and production. A way to achieve these aims is to work on new materials leading to a beneficial environmental impact. Therefore, it is possible to work on the performance, the reliability, the ecology and the recycling of the materials.

A car contains about 75% by weight of metals and 25% by weight of other different types of materials, as polymers, glasses, etc. It is possible to recycle or reuse a big part of them (in particular metals and glass), but in order to respect the new EU laws on the environment and recycling it is important to improve the recycling of the polymeric materials.

If we consider polymers, it is possible to say elastomers are 5% of the car weight and the most used are the SBR (Styrene-Butadiene Rubber), the NR (Natural Rubber) and the EPDM (Ethylene-Propylene Diene Monomer). Different car components, such as hoses, O-rings, tires, bushing, etc., are made of elastomeric materials. Considering their wide use in the sector, these materials are the subject of continuous research and development, in order to satisfy the carmakers new requirements (weight and cost reduction, performance, physical and mechanical properties increasing, etc.) and to develop and improve new recycling method.

This project focuses the attention on the possibility to recycle the processing waste of a real automotive component, made of EPDM sulphur based compound, via chemical methods and to use the recycled material to produce new automotive components.

For this aim, a real automotive component and laboratory slabs are produced and tested. Moreover, the processing waste of the specific component is used for the devulcanization process in order to obtain a new compound used for the production of new laboratory slabs.

A complete mechanical, chemical and physical characterization of virgin samples and recycled ones is performed. First and significative results concerning different tested materials are reported.

WS6 PO03

Sustainable materials for tyres. 1. Natural rubber compounds with better mechanical properties thanks to functionalized nanosized graphite

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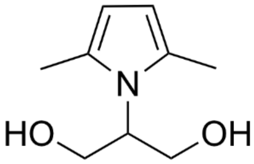
Natural rubber (NR), consisting in poly(1,4-cis-isoprene), is a highly stereoregular polymer. Its structure and properties actually make it the most important rubber, with a worldwide consumption of more than 12 million tons/year. The energy consumption required for the production of NR is much lower than the one required for producing a synthetic rubber: 8 vs 110 (MJ/kg) respectively. Also, the carbon footprint is lower for natural rubber: 0.4 vs 5 (kg CO_2/kg).

Nowadays it is clear that to have more sustainable materials for tyres, renewable sources should be preferred and therefore NR remains a material of primary importance.

This work was aimed at promoting better mechanical properties for NR - based compounds by using a carbon nanofiller, a high surface area nanosized graphite (HSAG) in particular. Nanocomposites were prepared with NR and HSAG where HSAG was either pristine or functionalized with a bio based janus molecule, 2-(2,5-dimethyl-1H-pyrrol-1-yl)-1,3-propanediol (SP), commonly named serinol pyrrole (HSAG-SP) (1). SP is depicted in the picture below.



Pristine HSAG nanocomposites were prepared through melt blending while those containing HSAG-SP were prepared through latex blending. Three levels of filler, 5.2, 15 and 24 phr, were used.

HSAG-SP lead to the following properties: a lower viscosity, a comparable vulcanization kinetics, a lower Payne effect according to shear strain sweep tests, better tensile ultimate properties and an improved fracture behavior. TEM analyses revealed that HSAG-SP allowed a better dispersion of the nanofiller in the rubber matrix. Such better dispersion was probably obtained thanks to the synergistic effect of the functionalization of HSAG and the preparation of the composite through latex blending. Functionalization therefore appears to be a promising tool for the reduction of the amount of filler in a rubber composite, allowing the design of lighter materials, which are required for a lower impact on the environment.

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WS6 PO04

Sustainable materials for tyres. 3. High aspect ratio natural fillers for rubber compounds with low dissipation of energy

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High compatibility of high aspect ratio nanometric filler with an elastomeric composite was achieved in this research using the chemical modification of the nanometric filler.

Rubbers cannot be used for any relevant application, even after crosslinking. Reinforcing fillers are required to achieve the required mechanical properties. Carbon black and silica are the traditional reinforcing fillers, largely used for rubber compounds for tyre applications. Increasing research efforts are for reinforcing fillers with nanosize, high aspect ratio and thus high surface area.

The research here reported was focused on a nanometric high aspect ratio filler, naturally occurring. Low cost clay mineral, easily available and with fibrillar structure, such as sepiolite Pangel S9, was selected as nanofiller. The research was aimed at improving the compatibility of sepiolite with the rubber matrix.

To achieve this goal, sepiolite Pangel S9 was treated with tetraethyl orthosilicate in the presence of basic catalyst obtaining amorphous nanosilica onto the surface of the filler. Sepiolite was also treated with HCl, removing different amounts of magnesium and obtaining a larger reactivity with the silane (triethoxy(n-octyl)silane) preserving the original fibrillar structure of sepiolite, used for promoting the chemical bond with the unsaturated rubber chains, through vulcanization.

Both modified sepiolites were used in NR based composites replacing a partial part of silica. With such chemically modified sepiolite, better dynamic-mechanical and static reinforcement were obtained for rubber composites based on diene rubbers such as natural rubber and poly(1,4-cis-butadiene) and silica as the main filler (1, 2).

Chemical modification and characterization of sepiolite, preparation and properties of rubber compounds are presented.

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WS6 PO05

Sustainable materials for tyres. 2. Biobased secondary accelerators for silica based compounds

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It is well known the sentence by Charles Goodyear: “There is probably no other inert substance the properties of which excite in the human mind an equal amount of curiosity, surprise and admiration” (1). He was referring to entropic elasticity. To have such a property, a rubber has to be crosslinked. Compounds for tyre application are crosslinked with sulphur base system. In particular, when silica is the reinforcing filler, the sulphur vulcanization package is composed by orthorhombic sulphur, at least a sulphenamide and a secondary accelerator, such as guanidines, thiurames, mercaptobenzothiazoles and others, in order to boost the reaction.

In this work, innovative chemicals were developed as secondary accelerators for silica based rubber compounds, starting from 2-amino-1,3-propanediol (known as serinol), which was used as such or as the starting building block for the preparation of imines (2). Imines, also known as Schiff bases, are traditionally synthesized from the reaction of primary amines with aldehydes or ketones, in the presence of an acid catalyst. This work had the aim to develop synthetic strategy to perform reactions for the synthesis of imines, by adopting reaction conditions inspired to the basic principles of green chemistry (3), in the absence of any solvent and catalyst, with aldehydes and ketones such as: acetone, cinnamaldehyde and camphor.

Serinol and serinol derivatives were thus used as secondary accelerators for the vulcanization of compounds based on silica and diene elastomers. Their behaviour was compared with that of diphenyl guanidine. Kinetics of crosslinking was studied, in the presence and in the absence of fillers. Dynamic-mechanical properties of the compound were determined. Extractability of vulcanizers from the compound was as well investigated.

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WS6 PO06

Sustainable isocyanate-free polyurethanes

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Polyurethanes (PUs) are among the most important polymers, with an annual production of more than 18 millions of tons, about 5 mass % of total worldwide polymer production. They are very versatile polymers, as they can be thermoplastic, elastomeric, thermoset and foams. They are suitable for a large variety of applications and, among them, as materials for cars. PU are formed by the reaction between polyols and isocyanates. Isocyanates present concerns from the point of view of their impact on environment, health and safety. They are produced from the reaction of amines with phosgene and have several potential negative effects on the human health.

The present work is based on the synthesis of isocyanate free-polyurethanes. Various strategies were adopted, such as:

(i) Ring Opening Polymerization (ROP) of cyclic carbamates prepared via dialkyl carbonate chemistry.

(ii) Ring Opening of cyclic carbonates by amines

The ROP of cyclic carbamates was carried out in the presence of boron trifluoride diethyl etherate as it resulted the most active catalyst. The process is solvent-free, chlorine-free and no by-products are produced. Furthermore, oligomers obtained with this procedure were modified at the chain end reaction with the biobased molecule 2-(2,5-dimethyl-1*H*-pyrrol-1-yl)-1,3-propanediol (SP). The so-formed PU-SP oligomers were used to prepare adducts with carbon nanotubes (CNT). The stability of the suspensions in ethyl acetate was observed and high-resolution transmission electron microscopy (HRTEM) micrographs showed that the PU oligomers are wrapped around the nanotubes.

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WS7–PLASTICS AND ENVIRONMENT

The focus of the public opinion on the negative effects of plastics on our environment has created the strong need of a clear answer from the scientific community on topics such as material recycling and reduction of the carbon footprint, during production and life cycle. Multiple and completely new cross competence research areas are being established all over the world. On top of this, legislation is also very active in trying to define strict directions that should protect and preserve our modern society.

Aim of the workshop is to bring together researchers and stakeholders from industry and society, to have a critical view on the complexity of the material life cycle and obstacles encountered during recycling. This would help into defining the current situation and create the bases for a better vision of the world we are contributing to shape.

WS7 - Organizing Committee and Conveners

- Paola Rizzo, University of Salerno
- Roberto Pantani, University of Saleno
- Daniele Caretti, University of Bologna
- Markus Gahleitner, Borealis Polyolefine GmbH, Austria

WS7 – Invited and Keynote Lectures

- **WS7 IL01** – Michael A. R. Meier, Karlsruhe Institute of Technology (KIT), Institute of Organic Chemistry (IOC), Germany "*Renewability is not Enough: Sustainable Synthesis of Biomass-derived Monomers and Polymers".*
- **WS7 IL02** – Alexandra Albunia, Markus Gahleitner, Susanne Kahlen, Borealis Polyolefine GmbH, Innovation Headquarters, Linz, Austria *"Polyolefin solutions for a sustainable future"*
- **WS7 KN01** – C. Cavalieri, G. Pellegatti, Basell Poliolefine Italia S.r.l. "Giulio Natta" Research Center, Ferrara, Italy *"How the innovative talent bridges polymerization technology, sustainable trends and customer needs"*
- **WS7 KN02** – Antonio Protopapa, COREPLA, Milano, Italia *"The new challenges in the recycling of plastic packaging"*
- **WS7 KN03** – Armando Galeotti, Versalis SpA, Mantova Research Center, Mantova, Italy "*Different ways to close plastic loop: the perspective of a polymer producing company"*
- **WS7 KN04** – Vincent Verney, Institut de Chimie de Clermont-Ferrand (ICCF) Universite Clermont Auvergne, CNRS UMR6296, AUBIERE, France "*Green Plastics Degradetion and circular economy"*

WS7 IL01

Renewability is not Enough: Sustainable Synthesis of Biomass-derived Monomers and Polymers

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In ages of depleting fossil reserves and an increasing emission of greenhouse gases, it is obvious that the utilization of renewable feedstocks is one necessary step towards a sustainable development of our future. In order to develop truly ˈgreenˈ approaches, using renewable resources is insufficient.[1] The available feedstocks rather have to be used in a sustainable fashion by combining as many of the principles of green chemistry as possible and by accessing and comparing the sustainability of chemical transformations. Within this contribution, new approaches for the synthesis of monomers as well as polymers from plant oils, [2,3] lignin [4] and carbohydrates will be discussed, thereby highlighting developed sustainable (catalytic) modification strategies. The focus of this presentation will be on novel approaches towards the sustainable functionalization of cellulose [5] and lignin, including new solubilisation and catalysis concepts as well as the use of multicomponent reactions.

For instance, a switchable ionic liquid, first introduced by Jerome[6] as well as Xie[7] for cellulose solubilisation, was studied and optimized[8] and later on applied for cellulose aerogel preparation.[9] The use and the advantages of this switchable solvent system for the preparation of various cellulose derivatives, for instance fatty acid cellulose esters (FACEs)[10] or cellulose succinylation with subsequent grafting via multicomponent reactions,[11] will be discussed in detail.

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WS7 IL02

Polyolefin solutions for a sustainable future

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The global population is still growing, constantly increasing the need to provide adequate food, infrastructure, mobility and health care for all these people. Connected to this demand, the question of material selection for these essential areas is critical, as global resources are already over-used today. The presentation will start with a global view on carbon footprint of European citizens, related to polymers as well as other materials and non-material related needs. Based on this, the excellent position of polyolefins – mainly polyethylene and polypropylene – in this respect will be highlighted. A number of application examples from simple to complex packaging solutions, infrastructure and mobility applications shall round of this introductory part.

From the perspective of the general public, these advantages appear to be overshadowed by the problem of plastic waste. The actual size of this problem in different areas of the world will be put outlined, followed by a roadmap on how to address it by structured collection and recycling on different levels. Finally, examples for mechanical recycling of polyolefins – in pure as well as mixed form – in different application areas will be shown.

WS7 KN01

How the innovative talent bridges polymerization technology, sustainable trends and customer needs

C. Cavalieri, G. Pellegatti

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LyondellBasell products, materials and technologies are found in almost all sectors of the economy and contribute to addressing modern challenges, including demographic growth, urbanization, healthcare, safety and food distribution. Our commitment to improving the quality of life is not less important, contributing to a more sustainable world through our program aimed at continuous technological and our product portfolio development.
Therefore, in our keynotes we would outline our company approach to sustainability and circular economy with some examples of products, solutions and technology.
The development of polymerization technologies has led to more simple processes with increased efficiency. With the development of the LyondellBasell proprietary technology called *Spherizone* a large portfolio of polypropylene products both of large consumption and of specialty can be produced, alongside some energy saving compared with the most widespread technology in the world called *Spheripol.*

In order to decouple the availability of plastics, in particular of polyolefins, from fossil feedstock, intensive efforts are geared to maximize the use of plastic wastes through mechanical recycling. Unfortunately, the current selection systems do not allow a perfect separation of polyolefins at reasonable cost. Therefore, we are going to have to enhance the mechanical properties of mixtures of polymers that are not always compatible, such as those ones containing a mix of polypropylene and polyethylene. Through our proprietary gas phase technology called *Catalloy,* which has the peculiarity to produce specialty products that can contain different phases of crystalline, amorphous and polyethylene polypropylene, we have developed high performance grades able to improve, as blending partner, the mix of polyolefins compatibility and to deliver then benefits in mechanical recycling of polyolefins.

WS7 KN02

The new challenges in the recycling of plastic packaging

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Plastic consumption in the world has achieved 350 Mn tons and 40% of this quantity is used for the packaging production.

In the last 20 years plastic packaging has seen significant improvement in terms of performance and materials but also their complexity has increased.
The quantity of easy to sort plastic packaging in the separate collection has gone down and, at the same time, packaging has become lighter and thinner creating significant problems to the end of life management.
Actual recycling technologies are hardly able to manage this complexity mainly when it comes to flexible packaging.

Furthermore, the new target suggested by the European Circular Economy package are also challenging: 100% plastic packaging must be recyclable and 55% recycled by 2030.

These results can only be achieved if all the value chain stakeholders will join the effort to identify proper solutions to make plastic packaging more sustainable: eco-design, chemical recycling, improved quality of separate collection are important actions to be considered.

WS7 KN03

Different ways to close plastic loop: the perspective of a polymer producing company

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The sustainable use of natural resources through Circular Economy models is becoming a factor of crucial importance for the next generations' future.

Nowadays, decisions and actions are urgent to avoid risks like, e.g., shallow waters pollution due to an uncontrolled end-of-life management of plastics. In this framework public authorities, especially in Europe, have outlined very challenging targets.

To make circularity and resource efficiency a reality, among the others, one of the most challenging paths to take is the research of alternative feedstocks. In this respect three ways can be depicted: Renewables (bio-sourced), Reduction (improving performance or service life) and Recycle.

Focusing on recycling, there are different options for managing the end-of-life of plastic materials like mechanical recycling (including an efficient logistic chain to reduce losses) and chemical recycling (to obtain monomers and building blocks).

According to the point of view of plastic polymers manufacturers, there are several ways to face these challenges, all of these are worth to be explored. In terms of costs/benefits ratio both ecological and economical point of view should be addressed in order to increase the sustainability of the plastic chain in the near future.

The answer to the challenges posed by EU directives will not be a single one, but very likely a mosaic of different solutions matching both technological aspects and organizational ones too. The final target is to fulfil materials performances as well as compliance to sustainability regulations.

WS7 KN04

Green Plastics Degradation and Circular Economy

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Plastics material are more and more attacked with regard to their environmental impacts. An alternative is in the development of green plastics which can be biobased or biodegradable or both, depending on their service time in use. Moreover, in the frame of the circular economy, it is also necessary to increase a lot the recycling rate of discarded fossil based plastic wastes. During all the steps of the service life a plastic material ages and undergoes oxidation reactions as the main degradation pathway through a set of radical macromolecular reactions. From a physical point of view, this evolution is accompanied either by molecular chain scission or by chain recombination. Sometimes, depending on the chemical nature of the considered polymer, both processes compete.

Un-controlled environmental exposition, as in the case of UV natural weathering, necessitates to be able to reach a very precise knowledge of the basic chemical degradation processes involved. In such a case the challenge is in being able to detect very weak amounts of changes at molecular scale. For that purpose, we use molecular rheology. This methodology is particularly convenient in the case of biobased/biodegradable (co)polyesters as the ester groups vibrations can hidden the determination of carbonylated by-products by Infrared spectroscopy. Moreover, it allows the deconvolution of the chain scission/chain recombination rates. The same methodology can be applied to plastic recycling to control the lifetime durability of recycled plastics by lowering the impacts of each processing step.

On the other hands, controlling the oxidative route may also be a promising way for (macro)molecular fractionation accompanied with a specific chemical functionalization. We develop a new-concept of photorefinery by using UV radiations as energetic input to initiate oxidation reactions. We can then take profit of that to do macromolecular chemical reactions in milder conditions.

Finally, this scientific knowledge can also be used to design new materials with intrinsic triggering of degradative processes to allow a time control of plastics recyclability.

WS7 - Oral Communications

- **WS7 OR01 –** Emilia Garofalo, Luciano Di Maio, Paola Scarfato, Antonio Protopapa, Loredana Incarnato *“Recycling of post-consumer flexible plastic films: a nanotechnology strategy to upgrade the material’s properties”*
- **WS7 OR02 -** Haroutioun Askanian, Nicola Schiavone, Sophie Commereuc, Vincent Verney *“Additive manufacturing and green polymer materials”*
- **WS7 OR03 –** Mariacristina Cocca, Francesca De Falco, Emilia Di Pace, Roberto Avolio, Maria Emanuela Errico, Gennaro Gentile, Maurizio Avella *“Microplastic Pollution: Sources, Quantitative Evaluation and Mitigation Strategies”*
- **WS7 OR04 –** Valter Castelvetro, Tarita Biver, Alessio Ceccarini, Mario Cifelli, Andrea Corti, Valentina Domenici, Stefania Giannarelli, Jacopo La Nasa, Tommaso Lomonaco, Enrico Manco, Francesca Modugno, Virginia Vinciguerra *“Tackling the present and future challenges for micro- and nanoplastics quantification and removal from polluted water bodies and related environmental matrices”*
- **WS7 OR05 –** Enrico Carmeli, Davide Tranchida, Dario Cavallo *“Application of thermal fractionation analysis for recycled polyolefin grades characterization”*
- **WS7 OR06 –** Federico Bella, Francesca Colò, Giulia Piana, Marisa Falco, Elisa Maruccia, Gabriele Lingua, Lucia Fagiolari, Giuseppina Meligrana, Claudio Gerbaldi *“Sustainable Matrices and Polymerization Processes for Post-Lithium Batteries”*
- **WS7 OR07 –** Carla Marega *“Effect of the collector on the mechanical properties of biodegradable and biocompatible PHB@MWCNTs elecrospun fibers”*
- **WS7 OR08**– Seif Eddine Fenni, Nacerddine Haddaoui, Orietta Monticelli, Dario Cavallo *“Renewable and tough poly (L-lactic acid)/polyurethane blend prepared by dynamic vulcanization”*
- **WS7 OR09 –** Raffaella Ferraioli, Luciano Di Maio, Paola Scarfato, Loredana Incarnato *“Valorization of pulper waste composites reinforced with basalt fiber”*

WS7 OR01

Recycling of post-consumer flexible plastic films: a nanotechnology strategy to upgrade the material's properties

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The advantages of flexible plastic packaging in reducing both food waste and package weight should be combined with robust end of life strategies. Unfortunately, flexible packaging generally consists of multiple material types that cannot be easily separated, thus posing several challenges from a recycling perspective (1).

The aim of this work was to improve the performances of Fil-s, a recycled material obtained from plastic flexible film waste that is made of polyethylene and a minor amount of polypropylene, with traces of polar contaminants (polyamides, maleic anhydride, etc). The idea was to upgrade the material's mechanical properties by application of a nanotechnology-based strategy that takes advantage of Fil-s composition.In particular, low amounts (2,5 and 5 wt%) of a virgin copolyamide (CoPA) and its nanocomposite masterbatch (CoPA+20%PM15), were melt compounded with this recycled material, in order to combine the advantages of the addition of a high performance plastic and the merits of polymer nanocomposites. Moreover, the nanofillers, acting as potential morphology-directors in a polymer blend (2), are also able to introduce new energy-dissipation mechanisms, resulting in enhanced stiffness-to-toughness ratio.

The good affinity between CoPA and Fil-s was proved by both spectroscopic and rheological analysis, and this led to a well refined morphology of Fil-s/CoPA systems, particularly in the case of the blend with the lower content (2,5% in weight) of CoPA. In fact, it was evidenced that this copolyamide amount was enough to saturate the interactions with the polar contaminants inside Fil-s, while a higher CoPA content tended to coalesce in the blend.

With regards to the hybrid mixture Fil-s+2,5%(CoPA+20%PM15), the balance of the tripartite interactions between the recycled matrix, the dispersed copolyamide phase and the organo-modified clay also resulted in a fine blend morphology. In particular, this latter was characterized by a narrower particles size distribution and a significant lower number of sub-micron CoPA droplets, compared to the unfilled corresponding blend Fil-s+2,5%CoPA. As a consequence, a more effective toughening mechanism (through craze formation) can be supposed for the nanocomposite blend Fil-s+2,5%(CoPA+20%PM15), resulting in a very significant increase in ductility (10 times higher) compared to the neat Fil-s, but without sacrificing the stiffness and the strength of the recycled material.

To the best of our knowledge, similar performances have never been obtained with recycled materials, in particular coming from flexible packaging waste stream.

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WS7 OR02

Additive manufacturing and green polymer materials

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In additive manufacturing, the material is added in layers until it takes the form of the desired product without the need for a forming tool. Furthermore, it produces less waste in the manufacturing process, thereby causing less damage to the environment. One of the most widely used technologies in this kind of manufacturing is fused deposition modeling (FDM), suitable for producing parts with complex geometries. However, a number of improvements are still necessary in order for FDM to fully evolve into a manufacturing tool rather than just a prototyping tool. One of the main improvements is related to the limited mechanical properties of the 3D-printed parts compared to injected material. Regarding this issue, many parameters could be taken into consideration, like the influence of filament orientation or raster angle, raster width, infill degree and layer thickness. Meanwhile, in the case of printing an object several times, there is a lack of information about the effect of printing order; the properties could differ, depending on whether the objects are printed individually or in a simultaneous batch especially with the grade of materials used in 3D printing (e.g. crystallization rate and kinetics).

Concerning the 3D printing materials, polylactic acid (PLA) is one of the most commonly used 3D printing filaments. PLA has low thermal stability, which limits its large-scale application. Paradoxically, the manufacturer-recommended temperature setting for PLA filaments in FDM technology is high (~200-230°C), and there is a limited amount of information concerning the effects of the thermomechanical processing involved in FDM. At the same time, the choice of polymer materials available on the market with large panel of properties is still limited compared to the materials available for conventional manufacturing processes, consequently, the development of new eco-friendly materials for new applications should be taken in consideration. For this reason, the valorization of pozzolan processing by-products have been investigated in this research as an eco-friendly composite with PLA matrice for use in 3D printing.

The purpose of this work, first of all, is to investigate the thermal degradation of PLA matrix, in injection molding and FDM processes, and to optimize the manufacturing parameters for FDM, particularly taking into consideration the printing order, with a view to improving the mechanical properties of the 3D-printed parts. Second, elaborate a new printable pozzolan based composite with adequate thermal and rheological properties for 3D printing technology, and optimize the 3D printing parameters to improve the mechanical properties of the printed objects.

WS7 OR03

Microplastic Pollution: Sources, Quantitative Evaluation and Mitigation Strategies

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In the last years, a growing concern has been arising about the contamination of marine ecosystems by microplastics, defined as plastic fragments smaller than 5 mm. Their impact on the environment is unpredictable and quite dangerous since they can adsorb organic pollutants and be ingested by marine organisms, potentially reaching the human food chain (1).

The washing processes of synthetic fabrics have been identified as one of the main source of microplastic pollution in marine environment (2). The mechanical and chemical stresses produced on the fabrics during a wash, cause the release of microfibres to wastewater. Due to their size, some of them are not blocked by the sewage treatment plants, reaching seas and oceans and becoming a threat for marine species. Therefore, understanding the effective contribution of the washing process of synthetic clothes to this environmental problem is of great importance. In this respect, two procedures were set up to evaluate the microfibre release during laundering performed at lab scale and in real scale washing tests (3, 4, 5). The effectiveness of these procedures have been assessed, and the procedures applied to identify the effect of different textile structures, laundering detergents and additives, washing conditions and parameters on the release of microfibres. The effective contribution of the washing process of synthetic clothes to microplastic pollution was determined.

Moreover, several mitigation strategies to reduce the impacts of microplastic pollution have been set up and tested. In details, new functional finishing treatments were developed with the aim to create a protective coating on the surface of synthetic fabrics, which reduces the amount of microfibres shed during a washing process and thus mitigating the environmental impact of microplastics. One of the treatments is based on the use of pectin, a natural polysaccharide present in the cell walls of plants (6); the other treatments were performed by using an electrofluidodynamic (EFD) methodto apply a homogeneous thin coating of biodegradable polymers on polyamide surface (7,8). In addition to surface treatments, new filtration systems for laundry machine were designed and their effectiveness to strongly reduce the amount of microfibres in wastewater was demonstrated.

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WS7 OR04

Tackling the present and future challenges for micro- and nanoplastics quantification and removal from polluted water bodies and related environmental matrices

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The alarming news concerning the pollution of freshwater and marine environments due to the dispersion of synthetic polymers and their degradation byproducts in the form of smaller debris and particles, the so-called *micro*- and *nano*plastics, is raising a growing concern among scientists, policy makers and common people. In fact, while the shocking images about the harmful effects on macrofauna of ingested or entangling macroplastics deliver a message that can be easily understood and connected to the presence of visible floating plastic items, the latter are possibly only the tip of the iceberg. The so-called Great Pacific Garbage Patch, with roughly 0.1 Mton floating macroplastics within the 1.6 million km^{2}of surveyed area (1), represents a very modest fraction of the 8 Mton of plastic waste input that is estimated to be dispersed in surface waters worldwide *every year* (2), or about 150 Mton ended up in the oceans since the inception of mass production and widespread use of synthetic polymer items (3). The missing part of the iceberg, possibly comprising a large fraction in the form of *micro*- and *nano*plastics, is likely to be found in the benthic and shoreline sediments as well as in the surface layer of the oceans, that is, where critical feeding and reproductive activities of aquatic organisms take place. The effects of microplastics on aquatic biota are still largely unknown, while there are clear evidences of their role as concentrators and carriers of persistent toxic chemicals and potentially harmful microorganisms (4).

From the above picture it is apparent the urgent need of affordable, accurate and selective methodologies for the sampling and the quantitative/qualitative determination of the elusive *micro*- and *nano*plastics from different matrices: marine and freshwaters, coastal sandy and mixed (with silt and biogenic components) sediments, benthic sediments, biota from aquatic environments as well as products of fisheries and aquaculture. On the other hand, a much more challenging task would be finding affordable, sustainable and effective solutions for environmental remediation.

Over the last two years we have been developing new methodologies for the isolation and characterization of the most common polymer types among microplastics found in marine and freshwaters (polyolefins, polystyrene, polyester, …). By adopting dedicated sampling procedures (to separate macroplastic fragments from environmental matrices further contaminated by micro- and nanoplastics) and multianalytical approaches including solvent extraction/fractionation, chromatographic (HPLC, GPC) separation with UV-Vis and fluorescence detection, hydrolytic depolymerization, Pyrolysis-GC/MS and other hyphenated thermoanalytical techniques, FTIR microscopy, NMR spectrometry and diffusometry, the polymer content indifferent matrices (spanning from sandy sediments to commercial fishmeal from processed fisheries products) and, to some extent, the degree of polymer degradation can be characterized (5, 6). In addition, the presence of adsorbed/absorbed toxic pollutants and the release of low MW volatile byproducts of polymer degradation under accelerated photoaging conditions are investigated. The results achieved so far as well as possible solutions for promoting microplastics degradation will be presented.

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WS7 OR05

Application of thermal fractionation analysis for recycled polyolefin grades characterization

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Recently much effort is being spent to acquire a knowledge on the properties of polymer materials sourced from recycling. In particular, for polyolefins, depending on the source, mixtures of polyethylene (PE) and isotactic-polypropylene (i-PP) in ratio of 10:90 or 50:50 wt% respectively can be found.

In general, the content and the composition of PE and iPP in a recycled grade is a valuable information difficult to obtain due to the complexity of these systems. Thus, molecular fractionation of recycled grades is an obvious approach in order to identify e.g. LDPE, MDPE, HDPE content in a complex blend. However, traditional fractionation methods, like Temperature Rising Elution Fractionation (TREF) and crystallization analysis fractionation (CRYSTAF), (1) are time-consuming, handlingtoxic solvents, and requiring expensive instruments. A promising route is represented by Successive Self-nucleation and Annealing (SSA) technique, (2, 3) which employs easy and inexpensive DSC methods and, thanks to the inherently fast crystallization behavior of polyolefins, can be carried out at high rates, substantially reducing the analysis time.

In this investigation we show the thermal fractionation results that can be achieved by applying the SSA protocol to different blends of recycled polyolefins. The large difference in melting points between the two main components has required the development of a tailor-made self-nucleation protocol, in order to separately study the detailed distribution of crystallizable sequence lengths of the two polymers. Thanks to the optimized thermal protocol, the recycled sample could be efficiently fractionated, highlighting the presence of iPP and PE chains with different crystallization capability, due to the different distribution of constitutional defects which break the regularity of the polymer repeating units.

Furthermore, a better interpretation of the results given by SSA on the recycled blends was achieved by applying the same fractionation protocol to single and blended model materials which mimic the actual recycled materials.

Finally a comparison between SSA results and solution-based fractionation techniques has allowed us to establish the limit of applicability of the former technique to these complex systems, and to effectively propose the method as a valid alternative to traditional and more established characterization methods.

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WS7 OR06

Sustainable Matrices and Polymerization Processes for Post-Lithium Batteries

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In recent years, large-scale energy storage systems are becoming extremely important to realize the load levelling of intermittent renewable energy sources, such as wind and solar, into the grid. Secondary (rechargeable) sodium-based batteries may represent the key enabling technology in this respect, because of high-energy density, low-cost, simple design, and easiness in maintenance. However, currently studied materials and processes are not in line with a truly sustainable point of view.

Here we offer an overview of our recent developments on innovative polymer electrolytes for sodium-ion batteries. In our labs, we develop different kind of polymer electrolytes by means of different techniques, including simple solvent casting (1) and UV-induced photopolymerization (UV-curing) (2,3), being simple, low-cost and easily scalable to an industrial level. All samples were thoroughly characterized from the physico-chemical and electrochemical viewpoints. They exhibited excellent ionic conductivity and wide electrochemical stability window, which ensure safe operation even at ambient conditions. Electrochemical performances in lab-scale devices were evaluated by means of cyclic voltammetry and galvanostatic charge/discharge cycling exploiting different electrode materials.

Our benchmark solid polymer electrolyte, when assembled in TiO_2-based lab-scale sodium cells, delivered a stable specific capacity of about 250 mAh g^{-1} at ambient temperature upon constant current cycling at 0.1 mA cm^{-2}. Its intrinsic stability was also confirmed by very long-term cycling test that exceeded 5200 h of continuous operation, which is definitely remarkable for a truly quasi-solid system.

Furthermore, we present emerging strategies aimed at identifying new polymeric matrices that can be integrated in a circular economy perspective. We propose sustainable matrices (even obtained from waste-recovery processes), and we demonstrate their ease transformation into electrolytes for sodium batteries to be coupled to renewable energy production systems.

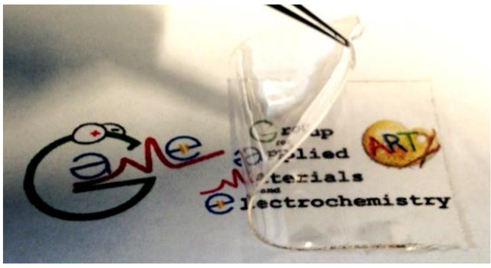

Figure 1. Digital photograph of a
UV-crosslinkedmethacrylic-based polymer electrolyte membrane.

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WS7 OR07

Effect of the collector on the mechanical properties of biodegradable and biocompatible PHB@MWCNTselecrospun fibers

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Poly(3-hydroxybutyrate) (PHB) is the most common and known among Polyhydroxyalkonoates (PHAs), optically active biopolyesters, synthesized by different kinds of bacteria.

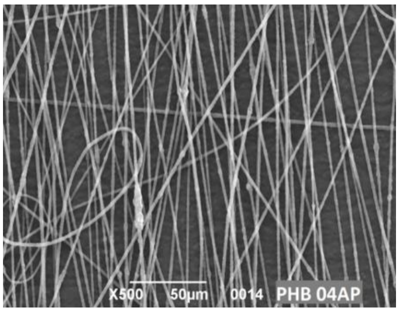
Poly(3-hydroxybutyrate) has mechanical properties like those of isotactic polypropylene, except for the elongation at break which is much lower and makes it a fragile and rigid material (1). So, it is of great importance to find ways to obtain this biopolyester with mechanical properties comparable to those of polypropylene.

Biodegradable and biocompatible polymer nanocomposites of PHB and multi-walled carbon nanotubes (MWCNTs) are obtained in the form of fibers by electrospinning.

Different amounts of MWCNTs are introduced in the solution of Poly(3-hydroxybutyrate) in order to study the effect on the properties of the final nanocomposites andto elucidate the influence of the collector on morphology and mechanical properties. In particular, the mats of aligned fibers should show better mechanical properties (2), amplified by the synergistic action of carbon nanotubes.

These types of composite materials can be used in a broad array of application such as scaffolds, drug delivery systems or wound healing, given the biodegradability and biocompatibility of these polymeric matrices.

The structure and morphology of PHB@MWCNTs nanocomposites are characterized by wide angle X-ray diffraction (WAXD), differential scanning calorimetry (DSC) and examined by scanning and transmission electron microscopy (SEM, TEM). The mechanical properties are measured and correlation with morphology is highlighted.



SEM image of aligned electrospun fibers

Image of the sample breaking (aligned fibers)

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WS7 OR08

Renewable and tough poly (L-lactic acid)/polyurethane blend prepared by dynamic vulcanization

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Melt blending of polymer is an effective way to achieve an attractive combination of polymer properties. Dynamic vulcanization of fatty acid based polyester polyol with glycerol and PLLA in the presence of Hexamethylene Diisocyanate (HDI) was performed with the aim of sustainably toughening PLLA (1). The dynamic vulcanization took place in a Brabender, leading to the formation of a PLLA/PU biobased blend. Melt torque, FTIR, and gel fraction analysis demonstrated the successful formation of vulcanized PU inside the PLLA matrix. SEM analysis shows that the PLLA/PU blends exhibit sea-island morphology. Gel fraction analysis revealed the formation of a rubbery phase, insoluble in chloroform, inside the PLLA matrix. The content of PU in the blends played an important role on the mechanical properties, the thermal stability, and the crystallization behaviours of the formed PLLA/PU blends. The overall crystallization rate of PLA was noticeably decreased by the incorporation of PU while POM analysis revealed that the presence of PU network inside the PLLA resulted in a faster PLLA nucleation step. The mechanical properties were enhanced by the formation of PU network; the impact strength significantly increased while the Young's modulus decreased. However, the thermal stability of the blends was slightly reduced compared to neat PLA.With improved toughness, the PLLA/PU blends could be used as substitutes for some traditional petroleum-based polymers.

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WS7 OR09

Valorization of pulper waste composites reinforced with basalt fiber

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In Europe, paper and paperboard are the most recycled materials, with a rate of about 85% but, at the end of the process, there is a rest, called pulper waste, composed by about 5% of cellulose and 95% of mixed polyolefins, in particular polyethylene (LDPE and LLDPE) and polypropylene (PP). At now this rest isn't recycled, it is just used for energy recovery, but plastic materials collected with paper that originate this waste can be recovered and reprocessed in order to find a second life application. This strategy is perfectly in line with the ambitious target set in the recent Circular Economy and with the zero waste politic (1).In any way, pulper waste presents worst mechanical properties in terms of rigidity and ductility. This aspect makes difficult to use the recycled material obtained from pulper waste in a commercial application in substitution of virgin polymers. One possible strategy to improve its characteristics and find a commercial application for this recycled waste is the addition of proper fillers and compatibilizing agents.

Actually, there is an increase in the use of eco-friendly, natural fibers as reinforcement for low cost polymer composites (2). Among them, one material of interest is represented by basalt fibers (FB), which is an inorganic fiber with very high modulus and strength, high temperature resistance, excellent stability and good chemical resistance; FB are easy to process, non–toxic, natural, eco-friendly, inexpensive (3,4,5).Moreover, if compared with other fibers, they offer exceptional properties over glass fiber (2).

Therefore, with the aim to improve mechanical properties of pulper waste, in this study we investigated the effectiveness of FB as reinforcing agent. In particular, the pulper waste was melt compounded with four different FB amounts (5, 10, 15 and 20 wt%), in a lab-scale double-screw extrusion plant, in order to study the effect of FB amount on the rigidity improvement. Pulper waste compounds at 20 wt% of FBwere additionally mixed with 25%, 50% and 75% of polypropylene coming from recycling of bumper (PPr), in order to further improve the mechanical behavior of the systems. All the samples were processed using a lab-scale single-screw extrusion plant, obtaining ribbons with a rectangular section, and were characterized by several techniques (TGA, DSC, FTIR, SEM, rheology, mechanical test) in order to obtain information on thermal stability, chemical interactions, morphology, rheological behavior, tensile and flexural properties. The obtained results revealed no detectable chemical interactions amongst the systems constituents. However, the FB addition enhanced the thermal stability of the samples and affected their rheological behavior, giving an increase of their dynamic viscosity. Moreover, the elastic tensile modulus of the compounded systems improved up to ca. 45% for samples containing 20 wt% of FB, and further beneficial effects arose from the PPr addition.

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WS7 - Poster Communications

- **WS7 PO01 -** Miriam Hubera, Vasiliki-Maria Archodoulaki, Markus Gahleitner "*Microplastics in aquatic ecosystems: How comparable are literature data?*"
- **WS7 PO02 -** Pierangiola Bracco, Federica Spina, Chiara Arcolin, G. Cristina Varese, Marco Zanetti "*Biodegradation of polyethylene by selected fungal strains*"
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- **WS7 PO09 -** Vincent Verney "*Circular Economy of plastic multilayer packaging: H2020 Terminus project*"
- **WS7 PO10 -** Babacar Niang, Nicola Schiavone, Haroutioun Askanian, Diène Ndiaye, Vincent Verney "*Effects of wood stem powder content on the morphological, rheological and thermomechanical properties of PLA matrix biocompositesnsert*"
- **WS7 PO11 -** Vissia Vitale, Antonio Vecchione, Roberto Pantani, Riccardo Bianchi, Giuseppe Milano, Gaetano Guerra, Sandro Del Giudice "*Optimization of PET grades and processing conditions for a lighter mineral water packaging*"
- **WS7 PO12 -** Francesco Prandi, Luca Guerrini, Stefano Cerini, Letterio Giannino, Daniele Caretti, Giovanni Mazzotti, Fiorenzo Parrinello, Fabrizio Pucci, Valentina Fiumi, Chiara Gualandi, Eugenia Sveva Stancari, Maurizio Fiorini "*Low molecular weight compounds in polyolefins: a comparative study of different analytical techniques and processing conditions*"

WS7 PO01

Microplastics in aquatic ecosystems: How comparable are literature data?

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The subject of microplastics as environmental contaminant is a relatively young one, but heavily reflected in the mass media and social networks. A majority of both popular and scientific papers in this area discusses the presence of small plastic particles in aquatic systems, like rivers (1), lakes and oceans (2). In order to get a realistic overall picture of the situation, a critical analysis of the available scientific literature with a clear focus on primary studies has been performed.

The target was to generate an overview of the available datasets in terms of concentration, size distribution and composition of microplastics in both fresh and sea water. Literature concerning the related sediments will be studied later (3). A general overview including differences resulting from the type of waters as well as the geographical location is presented. In addition, similarities or rather differences in the methodology of the various research groups are considered. Ranging from collection method through sample treatment to the evaluation and quantification methods, these differences quite obviously affect the reported results massively (4). In view of the present findings, it appears difficult to compare results from different groups without considering methodical differences.

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WS7 PO02

Biodegradation of polyethylene by selected fungal strains

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Improperly disposed plastic materials are a significant source of environmental pollution, potentially harming ecosystems .Polyethylenes (PEs) accounts for 30% of the total production of polymer materials, being the material of choice for a wide range of applications, including packaging, and their accumulation in the environment, along with that of other non-biodegradable polymers, is creating increasing concerns (1-3).

Widespread studies on the biodegradation of PEs have been carried out in order to overcome the environmental problems associated with PE waste (4). Since PE is considered to be practically inert, efforts were made to isolate unique microorganisms capable to promote PEs degradation. Although biodegradation of PE is widely recognized to be an extremely slow process, recent studies with selected microbial strains have shown promising results. Microbial enzymes are powerful tools for the biodegradation of PEs. Since the biodegradation activity of most enzymes is higher in fungi than in bacteria, fungal degradation of PE has deserved attention (3).

The purpose of this work was to study the degradation of PE by fungi isolated from plastics from landfills. Overall, 94 fungal strains were isolated and identified for their growth capacity in the presence of LDPE fragments as the sole carbon source. Starting from this first screening, 13 strains were selected and tested for their ability to degrade LDPE films. Degradation was assessed using qualitative analyses, i.e. ATR-FTIR spectroscopy and SEM observations, which allowed to evaluate the surface changes of PE. Furthermore, a semi-quantitative respirometric test was set up.

The respirometric test showed that all the 13 strains tested were able to use PE as the sole carbon source, albeit with different intensities, activating the fungal metabolism. The most intense respirometric activity was measured for two strains: *Fusarium oxysporum* and *Purpureocillium lilacinum*.

The SEM analysis after 30 days of incubation showed surface modifications of the PE filmby12 fungi; however, for 8 strains these alterations were not accompanied by evident changes in the FT-IR spectra associated to chemical modification of the polymer. On the other hand, 1 strain did not induce evident surface changes, but the appearance of an absorption band related to carbonyl moieties (1736 cm^{-1}) in the FT-IR spectra suggested that an oxidative phenomenon did took place on the polymer surface. Finally, for 4 fungi (*F. oxysporum and P. lilacinum*, in agreement with the respirometric results, and*Aspergillus fructus* and *Fusarium falciforme*) the SEM micrographs showed evident superficial alterations of PE films, accompanied by a very significant variation of the FT-IR spectra, with the appearance of intense absorption peaks related to carbonyl groups, suggesting a significant degradation activity.

In conclusion, this work demonstrates a first, promising step towards the isolation of selected fungal strains that show some degrading activity versus PE.

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WS7 PO03

Poly(styrene) and polyolefin micro- and nanoplastics insandy beach sediments: selective polymer quantification by GPC/fluorescence, and investigation on low MW environmental degradation by-products

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The increasing attention towards the plastic pollution in water basins and their sediment systems is stimulating efforts aimed at improving sampling and characterization procedures. In this context, the pollution of sediments by microplastics has been investigated less extensively than that of the water column, with analytical methods still being developed and requiring standardization and harmonization (1, 2).Microplastics dispersion in the environment is a consequence of their release into wastewater as primary particles, mainly from textile and personal care products, and of the fragmentation of larger plastic items caused by environmental degradation (photo-oxidative, hydrolytic) resulting in the generation of secondary particles. Commodity hydrocarbon polymers such as polyethylene, polypropylene, and polystyrene are those more likely to end up in shoreline rather than sea bottom sediments because of their low density (3). For these polymers environmental degradation occurs mainly through a photochemically assisted generation of oxidized functional groups (carbonyl, carboxyl, hydroxyl) followed by chain scissions and consequent reduction of the average molecular weight (4). These processes weaken the integrity of plastic items that become brittle up to their powdery disintegration (5). It has been suggested that these polymers may produce a substantial contribution in the pollution of coastal sediments since the processes of degradation and embrittlement of larger items are accelerated once they are deposited ashore, where photo-oxidative, thermal and mechanical stresses are greater (6, 7).Many of the analytical methodologies described in literature comprise the isolation and analysis of single microplastics fragments, limiting the minimum size of the fragment that can be reliably characterized and possibly excluding the extensively degraded ones, which may be more difficult to separate from the inorganic sediment or from biogenic debris.

Here we present a procedure based on gel permeation chromatography (GPC) coupled with diode array and fluorescence detectors, allowing selective semi-quantitative determination of polystyrene and partially degraded polyolefins, viz. the most common microplastics found in marine shoreline sediments. By operating the fluorescence detector at either 260/280 or 370/420 nm, the two polymers can be distinguished upon GPC separation of dichloromethane extracts. Expanded polystyrene (EPS) and oxidized low density polyethylene (LDPEox) (8) were used as reference materials for quantification of the microplasticscontent in sand samples from a marine beach in Tuscany, Italy. The main plastic pollutants were found to below-density polymers along with their partial degradation polymeric and oligomeric species (8, 9). Studies on the characterization and quantification of low MW by-products from different degraded plastics are also in progress. These are based on the analysis via Needle Trap Device-GC/MS of volatile compounds coming from degraded plastics debris and from polluted sandy beach sediments. A correlation between the level of oxidation as determined by ATR-spectroscopy and the amount of released volatiles in terms of quantitative and qualitative determination has been also tentatively performed.

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WS7 PO04

PET microfibers as ubiquitous pollutants of waters? A first sensitive and accurate method for their quantification in environmental matrices

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Microplastics (MPs) are introduced in the environment either as fragments from larger plastics (secondary MPs), or as-produced in particulate form (primary MPs). The former originates mainly from oxidative degradation of macroplastics. The latter are generally released in the washout of household waste by reason of their use in personal- and home-care products or as synthetic textile microfibers (1), especially poly(ethylene terephtalate) (PET) fibers. Recent data indicate that large amounts of polyester fibers are released by washing machines: approximately $6 \cdot 10^6$fibersweighing between 1.7 and 7.0 μg each are released by a 5 kg wash load (2). As a result, synthetic textile microfibers have been isolated in marine and freshwater environments, in the tissues of aquatic organisms (3,4,5) such as the *Daphnia magna* crustacean whose mortality rate was reported to increase as a consequence of such ingestion (6).Synthetic microfibers have also been identified in food products (7,8,9).

Contrary to polyolefins and polystyrene (the main sources of secondary MPs), PET has a lower propensity to photo-oxidative degradation. Nevertheless, all microplastics can be reduced to the so called "nanoplastics" (NPs, less than 1 μm) by further chemical and mechanical degradation processes that are accelerated by the large surface-to-volume ratio. Isolation of MPs and NPs from environmental samples is still an open issue, and only recently, efforts to set up methods for NPs detection and quantification have been reported (10). However, their sensitivity and accuracy is still quite poor.

In this contribution we present an analytical protocol for the identification and quantification of the total content of PET micro/nano-fibers and particles in environmental matrices. The procedure is based on the quantitative analysis of terephthalic acid (TPA) obtained by hydrolytic depolymerisation. The largely improved accuracy and lower limits of detection of TPA by means of reversed-phase HPLC with UV detector have also been validated by spiking samples from different matrices (marine and freshwater sediments, fishmeal from fishing industry) to assess possible interference from biogenic material.

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WS7 PO05

Control of chain walking by tailoring the strength of neighboring group interactions switches polymerization to dimerization catalysis

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Beyond the extensively studied high molecular weight polyethylenes, ethylene oligomers are also of practical importance. Recently, neutral κ2-(*N*,*O*)-salicylaldiminato Ni(II) complexes showed to be promising candidates (1,2). These Ni(II) catalysts convert ethylene to products whose microstructure showed to be strongly dependent on the catalyst structure and, in particular, on the size and on the nature of the ligand substituents, moving from high-molecular-weight polyethylene to hyperbranched oligomers to butenes (3). Detailed computational studies (4) showed that the linear propagation and termination/branches formation mechanisms overlap until the ethylene coordinates with the chain in cis to the oxygen ligand. Then, the reaction proceeds toward the new insertion or a monomer de-coordination. The de-coordination is the key step for a) β-H elimination and 2,1 re-insertion or b) chain transfer reaction. In the de-coordination transition state, the release of the monomer is promoted and made competitive by a weak coordination of the ligand to the metal center, operative only for the case of sufficiently electron-rich ligands. These studies initially performed on 2,6-(3',5'-$R_2C_6H_3$) substituted systems (Chart 1a) provided the right insights to extend the discussion to 'bridged' catalysts (Chart 1b) allowing us to rationalize the complete switch observed experimentally from polymerization do dimerization catalysis when OAryl groups are present in the 2,6 position of the salicylaldiminato motif (5).

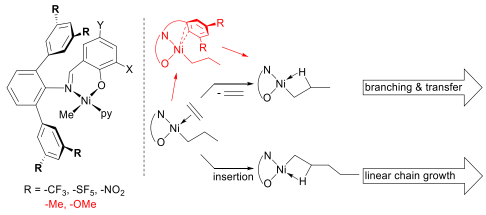

Chart 1a.

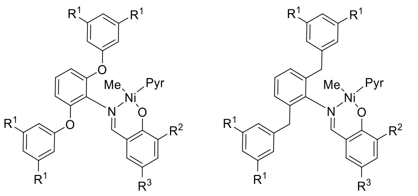

Chart 5b.

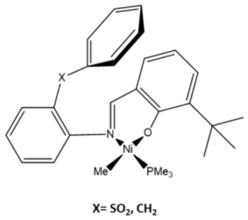

Chart 1c.

Encouraged by these results we decided to elaborate more the study including systems with other modifications of the ligand framework. One example we focused on is Ni(II)phenoxyiminato catalysts containing a remote ligand with a $–SO_2$- or a $–CH_2$- group (Chart 1c) that experimentally show remarkably different behaviors (6, 7).

All the results obtained, in agreement with experiments, lead to the same conclusions strengthening our new mechanistic hypothesis and paving the way for the scientific community to exploit this novel concept of design new catalysts tuning opportunely the Ni-ligand interaction on the base of the desired product.

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WS7 PO06

Nanoporous Crystalline forms of Poly(2,6-dimethyl-1,4-phenylene) for Removal of Pollutants from the Environment

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Nanometer-scale pores and capillary structures have long been studied because of their importance in many of the natural phenomena and their use in numerous applications (1). A more recently established process is the ability to fabricate artificial capillaries with polymers, which enabled new molecular separations and storage systems. In particular, syndiotactic polystyrene (sPS) and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) thermoplastic polymers have been received attention both in scientific studies as well as in industrial applications, owing to their peculiar nanoporous-crystalline (NC) nature (2,3). The structures of the NC forms of sPS have been well studied (4-6). For PPO, on the contrarythe crystalline structures of the NC forms are still unknown, mainly due to the absence of diffraction patterns of oriented samples (7).With this inspiration, we are exploring the structure and polymorphic behavior of PPO polymer, under uniaxial stretching at different temperatures and draw ratios. Some of the preliminary results (polarized FTIR) relative to uniaxially stretched PPO films are displayed in Figure 1.

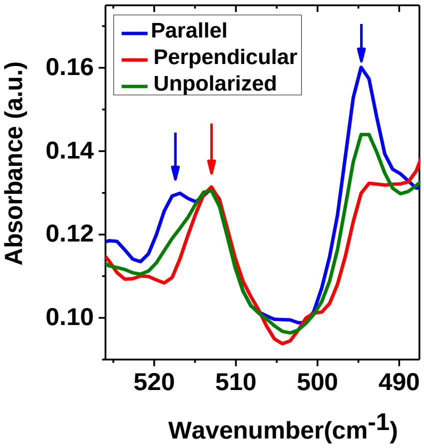

Figure 1. Polarized FTIR spectra for uniaxially stretched PPO film with a nanoporous-crystalline form.

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WS7 PO07

CO2 capture and sequestration by organic polymeric derivatives: two different approaches

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To meet the environmental change requirements, the CO_2 absorption and sequestration represents a sort of protecting shield in reducing the pollution and preserving acceptable quality life. A particular attention is promoted towards eco-friendly materials design, drastically reducing the environmental impact (1). We report here two different relevant approaches to contain this huge problem. The first is the preparation of nanoporous furfuryl-imine-chitosan fibers displaying appreciable absorption properties. Such an eco-material was obtained in a three-step procedure: (a) the chitosan-polyethylneglycol (PEG) fibers were obtained by electrospinning technique, followed by (b) washing the PEG towards chitosan fibers, and finally, (c) the imination with furfural in a heterogeneous system. The material displayed encouraging absorption capability, i.e. 1 mmol/g at 0.6 atm, noticeably improved as compared with unmodified chitosan fibers (1).

The second approach consists in the preparation of covalent organic framework (COF) reacted with $Re(CO)_5Cl$. COF product was obtained by condensation of melamine with benzene-1,3,5-tri-carboxyaldehyde. The resulting material contains linked Re, as shown by FTIR, NMR, and mostly ICP-AES analyses. Such powders are currently characterized to determine the effective CO_2 reduction, e.g. ciclovoltammetric examination. However, this material displays relevant CO_2 absorption power, namely about 3.4 mmol/g at 1 atm, near to values observed in metal organic frameworks (2).

Further improvements are oriented towards a possible use in membrane by checking in continuous columns.

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WS7 PO08

Isotactic 1-Butene-Ethylene Copolymers from Ziegler-Natta catalysis: Correlation between Microstructure and Formation of the Trigonal Form I

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A study of the crystallization behavior of isotactic 1-butene-ethylene copolymers (iPBEt-ZN) prepared with a Ziegler-Natta catalyst and having concentration of ethylene in a wide range from 9 mol% to 44 mol%, is presented. Because of the intrinsic heterogeneous nature of the catalytic sites these copolymers present a non-uniform distribution of the monomeric units and defects along the polymer chain, being constituted by mixtures of fractions consisting of chains with different composition and molecular masses. The different fractions have been separated by extraction in solvents with different boiling points and fully characterized.

The fractions of iPBEt-ZN copolymers show crystallinity even at high ethylene concentration. They surprisingly crystallize from the melt in form II of isotactic polybutene (iPB) up to ethylene concentration of 16 mol%. They crystallize in mixtures of form I and form II for concentration of ethylene around 14-16 mol% and do not crystallize from the melt but crystallize by aging at room temperature directly in form I, for higher ethylene concentrations. Crystallization of polyethylene has also been observed in copolymers with large ethylene content of 44-45 mol%.

The comparison with ideal model systems, represented by metallocene copolymers (1) (iPBEt-Met) having a controlled molecular structure with a truly random distribution of microstructural defects and comonomeric units along the chains, has shown that when the length of regular butene sequences is long enough common crystallization of form II occurs, whereas crystallization of form I is favored when the length of the regular butene sequences is short due to the presence of constitutional defects. In fact, for the iPBEt-Met copolymers a low concentration of ethylene units of nearly 2 mol% is sufficient to interrupt the regular butene sequences and promote the direct crystallization of form I from the melt and copolymers with 6 mol% of ethylene crystallize from the melt in pure form I. In the case of iPBEt-ZN copolymers, the observed crystallization of form II even at high ethylene concentrations is the hallmark of the presence of long regular crystallizable butene and of segregation of ethylene units in portions of the chains.

These results indicate that the study of the crystallization behavior may provide important information about the molecular structure of complex systems such as copolymers produce with Ziegler-Natta catalysts

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WS7 PO09

Circular Economy of plastic multilayer packaging: H2020 Terminus project

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Horizon2020 TERMINUS project (in-built**T**riggered**E**nzymes to **R**ecycle **M**ulti-layers: an**IN**novation for **US**es in plastic-packaging) addresses the challenge of unlocking recycling and reuse of flexible multi-layer and multi-compounds packaging materials used for food, beverages, cosmetics, pet food, fertilisers, any perishable goods in general. It will develop a range of smart enzyme-containing polymers with triggered intrinsic self-biodegradation properties, acting as adhesives or tie layers in the design and manufacturing of multi-layer plastics for food and non-food applications. The technology will be applied to biodegradable PUR-based adhesives for adhesive lamination and extrusion coating lamination, and polymers and tie layers (PBS, PLA, PPC or PCL) in blown extrusion.

TERMINUS will base its innovative and challenging objectives on a cross-disciplinary team of renowned organizations with expertise in enzymatic biodegradation of polymers, thermal protection of enzymes using nm organosilica and layered double hydroxide, cyclodextrins, UV and water triggered enzymatic activity, formulation of advanced polymers, manufacturing of multilayer plastic packaging, plastics recycling.

TERMINUS is based on TRL3 technologies and will reach TRL5. It will result in major market opportunities for European industrials in several well-established markets ready for market opportunities: plastic packaging (TPPS, STTP), industrial enzyme applications (BIOPOX), PUR adhesives (COVESTRO), biodegradable plastics (IPC), biotech plants (OWS), mechanical recycling (SIGMA). At least 15% of improvement of economic efficiency vs. current solutions (landfilling, incineration) is expected. A reduction of landfilling for multi-layer plastic packaging over 80% together with a reduction of overall plastic landfilling by 55% will be achieved with a minimum decrease by 65% of the overall CO2 footprint.

TERMINUS will be a breakthrough in reaching the 2030 European Commission objective to recycle 100% plastic packaging. The project started on January 1st 2019 and will last 49 months.

Terminus
https://www.terminus-h2020.eu/

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Effects of wood stem powder content on the morphological, rheological and thermomechanical properties of PLA matrix biocomposites

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Due to the demand by the consumer society of environmentally friendly materials, poly (lactic acid) (PLA) is a product derived from renewable resources, recyclable, biodegradable. It presents a good understanding between the promising properties and the cost. In order to increase mechanical and thermomechanical properties of PLA, PLA based composites from typha was prepared. The effect of typha content on the morphological, rheological, thermal and mechanical properties of matrix biocomposites (PLA) was studied. Three formulations were produced with different mass concentrations (25%, 35%, and 45%). The experimental results obtained show an increase in the rheological properties, as a function of the typha rod concentration. The DSC analysis showed an increase in the crystallinity rate of the various composites by confirming the nucleating effect provided by the filler. ATG analysis indicated a decrease in the decomposition temperature of the composites. Mechanical tensile tests had shown a significant improvement in the mechanical properties of the sample with a typha powder percentage of 45% (w/w) compared to the pure matrix.

WS7 PO11

Optimization of PET grades and processing conditions for a lighter mineral water packaging

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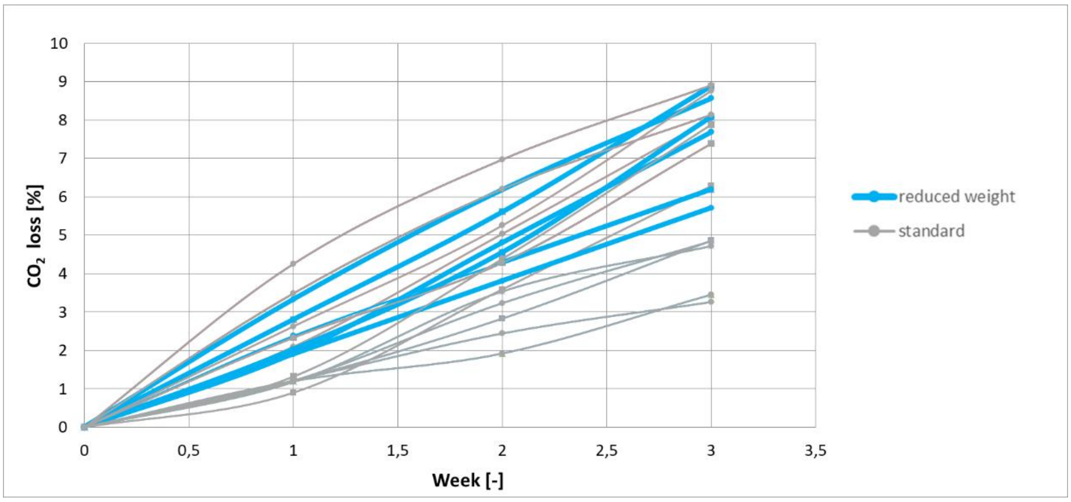
Packaging is a key factor of innovation and differentiation in mineral water markets. In the last fifty years there has been significant changes in the type of containers used for bottling. The success of plastic bottles and containers, present on the market since the sixties of the last century, is due to their lightness, lower cost and unbreakable behavior (1). The competition with glass has materialized with the polyethylene terephthalate (PET), suitable for food contact and in addition, unlike polypropylene and polyvinyl chloride, able to withstand the pressure of the carbon dioxide in carbonated beverages. Polyethylene terephthalate (PET) is a thermoplastic polymer belonging to the class of polyesters, characterized by high rigidity, and high melting point (Tm = 264 ° C), in comparison with aliphatic polyesters, due to the presence of the aromatic ring (2). The PET packaging offers an optimal combination of dimensional stability, transparency and barrier effect, in fact, it stands as a material of choice for the realization of bottles intended for the consumption of water, both flat and effervescent, and of soft drinks. Unlike other plastics, such as PVC, polyethylene terephthalate does not require the addition of plasticizers to increase its flexibility, so the problems related to the migration of these substances are absent in this case (3). Today, PET bottles represent about 90% of the total consumption of packaged water, especially in large formats for family consumption (1.5 and 2 liters). The company Lete aims to reduce the weight of PET bottles. To preserve the mechanical properties and the CO_2 barrier, studies have been conducted to optimize the PET degrees and the blowing process conditions. The study shows that by suitable selection of the grades of the pellets and of processing conditions lower-weight bottles can be obtained which present barrier to CO2 property comparable with those of standard bottles.



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WS7 PO12

Low molecular weight compounds in polyolefins: a comparative study of different analytical techniques and processing conditions

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A relevant problem of polyolefins processing is the presence of volatile and semi-volatile compounds (VOCs and SVOCs) such as linear chains alkanes find out in final products.

VOCs and SVOCs might arise from unreacted monomers and by-products of the polymerization process or could be the resulting products of undesired reactions occurred during storage, extrusion and moulding processes. This problem can be particularly relevant in recycled polymers.

These VOCs can be detected by customers from the unpleasant smelt and taste released into the packaging content and it can also be an environmental issue, at the same time they can cause negative side effects during process.

Since no previously standardized analytical techniques for polymeric matrix analysis are available in bibliography, we have implemented a method that implies different VOCs and SVOCs extraction and subsequent gaschromatographic analysis for quali-quantitative determination of such compounds.

In literature different extraction procedures can be found (1,2,3) including microwave extraction (MAE), ultrasound extraction (UAE) and thermo desorption (TDS) used with different purposes.

Each of the previous techniques possess some drawbacks and the obtained results are also related to some experimental setup.

Results obtained from TDS coupled with GC-MS equipped with a non-polar column show as by-products mainly linear chains oligomers with even number of carbon in a C8-C24 range (for HDPE).

In order to quantify these linear alkanes by-products, a more accurate GC-FID determination with internal standard has been run on MAE extracts.

The correct combination of solvent, extraction temperature and time is a crucial point in order to obtain reliable analytical results and a deep study has been carried out in order to find the best analytical conditions.

In general, low amount of VOCs have been evidenced inside the pristine polymeric samples, the amount of the low molecular weight product is not increased during the processing but a significant reduction is frequently observed especially when vacuum is applied during the extrusion process.

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WS8 – SMART MATERIALS

The workshop addresses the new opportunities given from science and technology of materials to sustainability of industry and society, with presentations of new possibilities and tools, rather than just scientific results, which can open new perspectives in this direction and mutual integration of research and production worlds. Although not limited to only the following topics, the focus of the workshop will be on six main aspects, which are highly cross-sectorials:

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- **WS8 KN01** – Radek Zbořil, University Olomouc, *“Low-dimensional carbon nanostructures for biomedical, magnetic, and environmental technologies*”
- **WS8 KN02** – Silvia Marchesan Università di Trieste *“Nanostructured materials for selective chemical separation and advanced diagnostics”*
- **WS8 KN03** – Paolo Vacca R&D Manager, SAES Getters S.p.A, viale Italia 77, Lainate (MI) Italy *“Functional composites for advanced packaging solutions”*

WS8 KN01

Low-dimensional carbon nanostructures for biomedical, magnetic, and environmental technologies

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Covalent and non-covalent chemistry of 2D graphene and 0D carbon quantum dots opens the door to smart materials involving non-metallic magnets, single-atom catalysts, advanced biosensors, or theranostic agents (1–4). A general synthetic strategy enabling to prepare a new family of 2D materials based on nucleophilic substitution of fluorographene will be presented (5, 6). Nitrogen substitution in the graphene and carbon dot structures will be discussed as a tool for precisely tuning their magnetic and photoluminescence properties along with switching the spin state of molecules (7–9). Carbon dots will be explored as advanced 0D materials for cell labelling, nanothermometery inside living cells, optical imaging, and anticancer photothermal therapy. Enormous application potential of recently discovered 2D materials, cyano-graphene, and graphene acid is manifested via their exceptional affinity for binding single atoms and molecular species (10, 11). Such hybrids are highly efficient in environmental technologies including noble metals recovery, catalysis, prevention of bacterial resistance to silver nanoparticles, and the development of sustainable molecular magnets. Finally, non-covalent hybrids of 2D-graphen-based materials and metal organic frameworks (MOFs) will be introduced as superhydrophobic/oleophilic nanofibrous and hierarchical superstructures enabling the separation of oil fractions and organic solvents from water (12, 13).

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WS8 KN02

Nanostructured materials for selective chemical separation and advanced diagnostics

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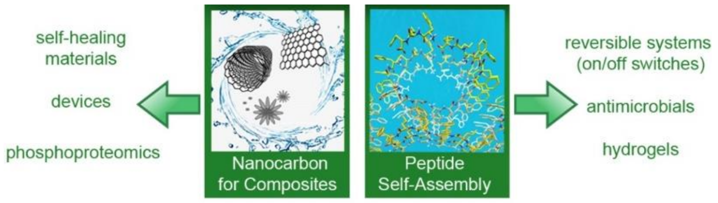
Nanostructured materials provide superior performance than conventional matrices to address various application challenges in medicine (1,2). Our research focusses on the tailoring and development of nanostructured materials for use in aqueous systems and green solvents, taking advantage of the unique properties of: i) carbon-nanostructured based composites, and ii) supramolecular systems based on self-assembling peptides or their analogues, to achieve functional smart materials. In the field of diagnostics, phosphoproteomics offers a powerful approach for the multiple detection of phosphopeptide biomarkers, which can provide a comprehensive picture of deregulation of signaling processes, a hallmark of pathological states and malignant transformations. Unfortunately, phosphopeptides' transient nature makes them a challenging target analyte. A winning strategy consists of the combination of NanoHPLC-MS/MS and nanostructured magnetic solid-phases to selectively enrich phosphopeptides from complex biological samples (3). These smart naanocomposites can be used for magnetic separation, while changes in the carbon scaffold nanomorphology results in different selectivity and target affinity. In areas that span from smart coatings to chemical separation, self-assembling (tri)peptides are low-cost, convenient building blocks for biodegradable smart materials. Their durability can be fine-tuned by design, *e.g.*, by appropriate combination of L- and D-amino acids (4). These systems can undergo reversible assembly-disassembly cycles, upon application of a variety of stimuli, including light, heat, or pH. In this manner, their function can be switched on/off as required. For instance, they can be used to achieve antimicrobial (5), biocatalytic (6), or drug-delivering (5,7) hydrogels. They can also be combined with metal-organic cages that entrap molecular cargo selectively. In this way, a mixture of small molecules can be separated by diffusion through sequential layers of gel, whereby a different cage entraps a different guest in each layer (8). Alternatively, combination of carbon nanotubes and self-assembled peptide fibrils can yield self-healing materials. As the library of self-assembling simple peptides expands, so do the potential applications of these smart, biodegradable systems (9).



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WS8 KN03

Functional composites for advanced packaging solutions

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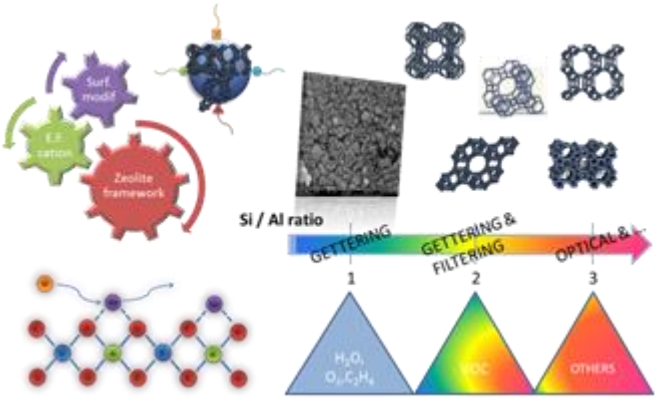
New approaches for efficient packaging solutions are continuously under scrutiny to ensure longer shelf life coupled to safety store conditions. The development of new materials is a fundamental step in introducing innovative functions in conventional configurations where knowledge intensive approaches need relevant efforts in R&D activities. For the last seventy years, SAES core technologies have enabled the preparation of innovative materials to meet the customer needs in several industrial application up to the more recent definition of an innovative technology platform based on Functional Chemicals. Starting from the SAES getter technology, new approaches have been designed to developed a set of innovative functional composites: engineered nanozeolites, submicro metal-oxides, adsorbing polymers and polymer capsules area adopted to produce innovative systems for advanced packaging solutions where new functional properties in terms of solid-gas interaction for both VOC adsorption/releasing and gas permselectivity are introduced. These materials represent a tremendously versatile and promising platform to prepare new systems with tunable reactivity and to enable their efficient integration in proprietary organic formulations. Three products will be described in terms of synthetic routes, composite designing and materials processing to meet application requirements ranging from organic electronics to advanced packaging.



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- **WS8 OR01 –** G. V. Bianco, M. Grande, A. Sacchetti, P. Capezzuto, M. Scalora, G. Bruno "*Graphene technological applications: chemical strategies to overcome limitations*"
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- **WS8 OR07 –** F. Nardelli, F. Martini, E. Rossi, M. Geppi, L. Calucci, S. Borsacchi, M. Cettolin, A. Susanna, E. Carignani "*Structural and dynamic characterization of elastomeric materials by time domain NMR spectroscopy*"
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WS8 OR01

Graphene Technological Applications: Chemical Strategies to Overcome Limitations

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Graphene is gaining increasing technological interest due to its broad applicability from electronics, photonics, photovoltaics and sensoristics to biomedical devices and to a variety of structural applications. The majority of graphene applications take advantage from the unique combination of transparency, conductivity and flexibility. These three properties represent the "*graphene core-values*" that identify univocally graphene (defined as a single sp^2 carbon layer) in the landscape of graphene-based materials (graphene oxide, reduced graphene oxide, graphene nanoplatelets, etc.). Although many graphene applications have been experimentally demonstrated (1, 2), the technological transfer from laboratory to industrial scale is still limited. The reasons are related to both production cost and to the quality of graphene currently available.

The discovery of the metal-catalyzed chemical vapor deposition, CVD, methodology (3) opened the way for the large scale growth of single layer graphene. However, CVD graphene layers are polycrystalline and, the morphology/structure at atomic level is well far to be free of defects, which affect graphene properties. These defects are often perceived as performance limiters, but in the case of graphene their chemical functionalization can help overcome the current material limitations.

The talk will touch on topics that are explored in our lab: CVD graphene growth and transfer on substrates, graphene doping and functionalization (4). We will present chemical processes that effectively act as "*point-defect healing*" resulting in: (i) high quality graphene layers, (ii) tuning of the graphene electrical transport properties and (iii) p-doping of graphene to very low sheet resistance. Last results on graphene-based devices, from solar cells to sensors and transparent antennas will be presented to validate our chemical strategies for tuning graphene properties.

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WS8 OR02

Smart Materials at the service of Artificial Intelligence

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Artificial Intelligence is having an enormous impact on our societies. There are two strategies to develop Artificial Intelligence. A strategy consists in writing human-like intelligent software running in computers or special-purpose hardware. The other strategy is neuromorphic engineering that implements surrogates of neurons, through non-biological systems, for either neuro-prosthesis or the design of brain-like computing machines (1, 2). Surrogates of neurons can be implemented by either solid materials in hardware or solutions of non-linear chemical systems in wetware. In our research group, we are pursuing this second approach. We use Molecular, Supramolecular, and Systems Chemistry to mimic some basic performances of the elements of the human nervous system (3, 4). Stimuli-responsive materials are chosen as surrogates of sensory cells. For example, we have developed a system of photochromic compounds, which extends human vision from the visible to the UV (5, 6).

We have devised elementary artificial networks, based on oscillatory chemical reactions and photosensitive compounds, which communicate through UV-visible signals and give rise to phenomena of temporal self-organization analogous to those of real neurons (7, 8).

Finally, we have implemented a composite system, made of a pH-sensitive gel and dialysis membrane, working as an artificial gland model (9).

The sensory, neural, and actuator systems we have devised can be used as modules for futuristic Chemical Robots. A Chemical Robot is thought to be a molecular assembly that reacts autonomously to its environment through molecular sensors, makes decisions by its intrinsic artificial neural networks, and performs actions upon its environment through molecular effectors. The design of the elements for Chemical Robots blazes the new trail of Chemical Artificial Intelligence.

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WS8 OR03

Smart electro- and photo-catalysts based on nano-carbon hybrids

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Carbon nanostructures have established themselves as popular components in the assembly of multi-component smart materials in a variety of applications (1). We have exploited the properties of carbon nanostructures to assemble carbon-inorganic nanohybrids with a remarkable performance in catalytic reactions related to energy applications and environment. Appropriate synthetic conditions allow access to structures where the synergy between the conductive nanocarbon scaffold and the inorganic phase is a key parameter for enhanced electrocatalytic activity in processes such the CO_2 reduction (2) and the hydrogen evolution (3). Moreover, modification of the carbon nanostructure by incorporation of magnetic components allows a powerful selection process of the most active phases, as demonstrated for the photocatalytic H_2 production from biomasses (4). Finally, we proved that smartness of the nanocarbon catalyst can be also effected without adding any metal component: we prepared metal-free carbon nanostructure-based materials that have set a new benchmark for the sustainable synthesis of a key industrial molecule such as hydrogen peroxide (5). The role of the nanocarbon and the importance of securing an appropriate interfacing between the various component has been investigated in most cases.

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WS8 OR05

Functional materials from nanocellulose

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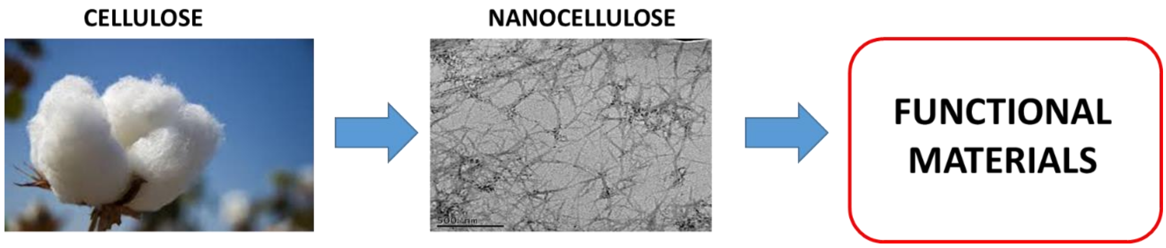
Nanocellulose is one of the most promising biocompatible materials due to its particular properties, renewability, and abundance (1). Innovative functional materials can be obtained from nanocellulose. They can find applications in different fields including bioremediation and biomedicine.
This presentation aims to show some recent advances on this topic obtained by the INSTM local unit at POLIMI (2,3,4,5,6,7).



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WS8 OR06

Cyclodextrin-based Polymers as Efficient and Reusable Adsorbents to Remove Emerging Pollutants from Water to Promote a Sustainable and Circular Economy

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Currently, emerging contaminants are a matter of great concern about water pollution. The high interest towards these compounds is due to the high risks they confer to the aquatic ecosystem, even though they are present at low concentrations (1). Emerging pollutants include personal care products, drugs, pesticides and solvents, which are persistent, potentially carcinogenic and endocrine-disrupting even for humans (2). As a facile approach for emerging contaminants removal, the adsorption technique onto cyclodextrin-epichlorohydrin water-insoluble copolymers was investigated; the herbicide atrazine and the antibiotic sulfamethoxazole were chosen as model pollutants for this purpose. The adsorbents were characterized through FTIR-ATR spectroscopies, SEM and DSC analyses. In-batch adsorption experiments were performed, to assess the influence of several physico-chemical parameters on the pollutant removal efficiency, i.e. contact time, adsorbent dosage, initial atrazine concentration, pH, ionic strength and temperature. Both for atrazine and sulfamethoxazole, a significant removal was obtained within only 30 minutes of contact with the adsorbent. The adsorption isotherm, thermodynamic and kinetic analyses give information about the process, mainly involving weak and reversible interactions, including H-bonds and van der Waals forces, along with the potential formation of host-guest-like inclusion complexes between the pollutants and the polymers, as suggested by FTIR-ATR spectroscopy and DSC analyses. Good atrazine desorption efficiency was obtained through extraction with methanol, while sulfamethoxazole was totally desorbed in water at 80 °C. Moreover, the polymers could be re-used at least for 5 times without significant losses in their efficiency; so, they can be easily regenerated in view of a circular and sustainable economy. In-flow adsorption experiments are in progress in our laboratory and the possibility of photodegrading the pollutants adsorbed onto the material is being evaluated, by including TiO2 inside the cyclodextrin polymers structure, exploring the effects of the Advanced Oxidation Processes.

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WS8 OR07

Structural and dynamic characterization of elastomeric materials by time domain NMR spectroscopy

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In the last decades, many efforts have been dedicated to the improvement of the mechanical properties of elastomeric composite materials, as they are particularly attractive for several industrial applications. As a matter of fact, these properties are mainly related to the motional constraints of the polymer network, which are due to the presence of physical entaglements and chemical cross-linking between polymer chains, and may be influenced by the presence of different additives and reinforcement fillers (carbon black, nanosilica, clays) (1,2). Usually, the cross-link density is monitored by mechanical measurements (modulus, strain at stress, etc.); however, these methods provide only macroscopic observables, but are not suitable for a description of the topology and dynamics of the polymer network at the molecular scale. Indeed, this knowledge is required to have a more complete view of the factors that correlate with the mechanical properties of elastomers and, consequently, to better address the design of optimized materials. In this context, low field ^{1}H time domain (TD) NMR can give an important contribution (3).

In this work, we have investigated the effect of the formulation (polymer, additives, filler) and the vulcanization conditions on the structural and dynamic properties of different elastomeric materials, with application in the tyre industry, by a combination of TD NMR methods. 1H Multiple Quantum (MQ) esperiments (4) were used to evaluate the residual 1H-1H dipolar couplings, which arise from the fast anisotropic motion of the polymer chains and are thus directly related to the amount of topological contraints within the polymer network. 1H relaxation times (T_1, T_2) (5) were measured to probe a wide range of motional frequencies of the polymer chains. In particular, ^{1}H spin-lattice relaxation times (T_1) were evaluated by means of Fast Field Cycling (6) experiments at different temperatures, covering Larmor frequencies from 10 kHz to 35 MHz.

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WS8 OR08

Tailoring materials properties from nano to microscale

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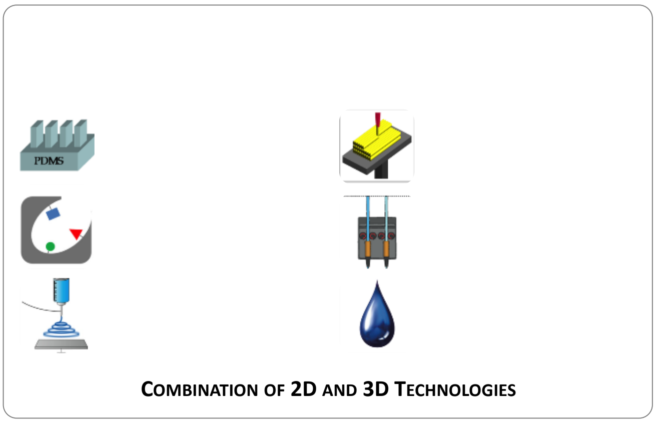
A biological tissue is a composite material with "bottom-up" hierarchical structure that is closely related to its heterogeneous function. The extracellular matrix modulates biochemical and biophysical signalling, and its rigidity is an important microenvironmental parameter that regulates the spatiotemporal dynamics of intercellular signalling. For this reason, many studies are focused on fabricating scaffolds processed at multiple scales with structural and mechanical properties that are optimal for eliciting specific response or mimic those found naturally. These scaffolds have to present large surface areas that have appropriate topology and biochemical cues (e.g, ligands) at the nanoscale for tissue adhesion, while also exhibiting integral porosity to allow for the exchange of molecules that maintain cellular function. The combination of multiple techniques, materials and cell types is a novel trend in Bioprinting, in order to fabricate constructs, which can mimic the geometry, complexity and functions of human tissues [1-3]. Currently, this research field is experiencing a rapid transformation from basic research to emerging industry [4]. The market growth is expected to be driven by new printing technologies, as well as the expansion of new applications beyond the medical field [5]. Although the technology has reached the commercialization, the integration of multiple printing techniques is far from being reliable: several researches on multi-material scaffolds are based on the consecutive use of different bioprinters with different technologies [1]. In this study several applications of different combination of polymer processing methods will be proposed in order to tailor a material from milli to nano scale and develop an in vitro functional model of human tissue.

Multitailoring process



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WS8 OR09

Smart natural hydrogels for biomedical applications

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Introduction

Smart hydrogels reversibly change their properties when exposed to an external driven force as pH or temperature variation (1). Methylcellulose (MC) is a polysaccharide derived from cellulose and when dissolved in aqueous solvents it forms reverse thermo-responsive smart hydrogels that undergo a sol-gel transition when heated (2). At the same time, another smart material is represented by gelatin that needs to be crosslinked for biomedical applications. Crosslinked gelatin bulk scaffolds, 3D printed structures and microspheres can be obtained by tuning its crosslinking kinetic, innovatively without the need of post-curing or external treatments to stabilize the crosslinked printed hydrogel structure (3).

Possible applications in regenerative medicine of MC-based hydrogels as well as crosslinked gelatin hydrogels are here described.

Materials and Methods

MC-based hydrogels. METHOCEL powder 8% w/v was dissolved at 55 °C in different distilled water saline solutions: phosphate buffered saline at two different concentrations (MC_PBS10 and MC_PBS20), sodium sulfate 0.05 M (MC_Na005) and 0.1 M (MC_Na01) and distilled water as control (MC_water). After complete powder dissolution, solutions were sealed in petri dishes and stored at 4 °C for 24 h to allow MC complete hydration (2).

Crosslinked gelatin hydrogels. Gelatin hydrogels (GEL) were crosslinked by a Michael-type addition by mixing gelatin type A from porcine skin (15% w/v) and methylenebisacrylamide, MBA, used as crosslinker (23.3 mg), to initiate the crosslinking reaction. Different hydrogels were prepared by varying gelatin concentration (i.e., 15 or 25% w/v) and the crosslinking reaction stoichiometry (i.e., MBA: gelatin amines = 1:1 or 0.5:1).

MC and gelatin hydrogels were investigated by investigating their chemico-physical, mechanical and in vitro biological properties. 3D printing was also investigated for both the smart hydrogels.

Results and Discussion

MC-based hydrogels. Rheological and UV-spectroscopy tests showed that the addition of salts to MC hydrogels allowed lowering the LCST of the MC hydrogel; moreover, hydrogels produced in 0.1 M Na2SO4 or PBS 20 g/L were proved to be particularly promising for cell sheet engineering application, showing a LCST below 37 °C. Extrusion-based 3D printing was shown to be an effective strategy for cell sheet engineering, having a desired shape using MC-based hydrogels as ink, with the ultimate goal of the regeneration of complex tissues.

Crosslinked gelatin hydrogels. The physico-mechanical properties of chemically crosslinked GELs were successfully tuned by varying gelatin concentration and reaction stoichiometry and allowed identifying the most suitable formulation (15GEL05) as soft tissue substitute. Moreover, the cytocompatibility of GELs was proved and the ability of GELs in supporting cells attachment and proliferation make the proposed hydrogel a valid material as soft tissue substitute. 15GEL05 was successfully printed by tuning the crosslinking kinetic the printing process optimization. The obtained 3D porous scaffolds proved to be suitable as supports for soft tissue regeneration.

Conclusion

Smart hydrogels showed appropriate properties for applications in regenerative medicine by tuning their properties.

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WS8 OR10

Smart Multifunctional Nanomaterials based on Colloidal Nanoparticles for Biomedical Applications

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In the last years the extraordinary advances in the field of material science and, in particular, in nanomaterial synthesis have resulted in a great potential for biomedical applications.

A variety of preparative and post-preparative colloidal routes have demonstrated able to obtain a wide choice of inorganic nanoparticles (NPs) and nanocrystals (NCs), with different compositions, that can be achieved with a high control on size, shape and surface chemistry, ultimately tailoring their electronic, optical, magnetic, thermal and chemical size dependent properties. Functionalization strategies allowing to surface engineer NPs and NCs and to tune their specific chemical reactivity towards the surrounding environment, have enabled their conjugation and combination with biologically relevant entities, thus producing advanced smart materials for diagnostics and therapy.

Here the design and fabrication of specialized nanomaterials ingeniously combining suitably functionalized NPs and NCs, such as semiconductors, plasmonic and magnetic nanostructures, with peptides, drugs and other relevant biological systems will be presented (1-3) and their potential for diagnosis and treatment of different diseases, including cancer and neurodegenerative diseases will be illustrated. In particular, examples of drug delivery, labelling and theranostics multifunctional systems, based on NIR photoactive nanomaterials, plasmonic nanostructures and magnetic NPs will be reported (4-5).

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WS8 OR11

Polymeric microneedles based devices: from material design to application

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Modern approach to healthcare is largely mediated by economic factors since public health budget is in constant growth in all the Western nations. The aging of the population also increases the minimum needs and the hospital admissions rate (1). Many possible solutions have been proposed to face this big problem from every possible side: for example, food awareness campaigns, mass vaccinations, diagnostic screening by age group. Every large scale initiative sees its effectiveness greatly reduced by the intrinsic limits of traditional medicine, based almost exclusively on clinical practice supported by statistical studies and on pharmacological chemistry (2). The next revolution in medicine, and more generally speaking in healthcare, will come from innovative technologies acquired from very different field of applications, such as large electronic consumer and telecommunication, and adapted to specific problems (3). In particular, micro- and nanotechnologies, i.e. systems and devices having dimensions under 10^{-6} m, are driving the development of new products more performing than the existing ones. Scaling down the size of common materials, both the organics and the inorganics, it is not only matter of fabrication ability, but it opens the way to a completely diverse world where things behave different (4). In some cases, the matter properties drastically change on the nanoscale. Crystalline silicon, the basic material in electronic, is not light emitting and can cause silicosis, a pulmonary disease, whereas its nanostructured counterpart, the porous silicon, is photoluminescent and completely biodegradable; carbon is highly insulating, since it has a very large bandgap, while carbon nanotubes and graphene are highly conductive; and the list of examples could continue for a long. In other cases, such as the one of popular microfluidics, geometrical features matter more than bulk properties. As a matter of fact, when linear dimension (L) decreases, surfaces are more important than volume. Moreover, due to the intrinsic difficulty of translating laboratory science into industrial production, most of the scientific discoveries found in the academic habit is lost in a “Death Valley” before industry could get advantages from them. In this view, technology transfer companies play a strategic role in overcoming the gap between scientific research and industrial development. In South Italy, Materia’s S.r.l. is one of the most active start-up company highly specialized in technology transfer In this work, we will focus on a specific system, developed in collaboration with academic institutions, that is explicative of brand new technologies applied to human healthcare: the polymeric microneedles. Materia’s Srl has patented two technologies for fabricating MN by using a photolithographic approach (5). These devices can be added with a porous silicon free-standing membrane, using, for example, polyethylene glycol (PEG) or other biodegradable polymers and a commercial photo-catalyzer (6).

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WS8 OR12

Stimuli-responsive materials towards biological applications

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Regeneration of muscle functionality is a major challenge for medicine; the design of biocompatible artificial muscles, able to contract and generate tension in response to external stimuli, would represent a possible strategy to effectively address it. Liquid crystalline elastomers (LCEs), in this sense, represent a class of smart polymers meeting the necessary requirements to obtain biomedical devices able to assist the damaged muscular contraction (1-4). LCEs borrow from liquid crystals the orientational order at a molecular level and the responsivity to external stimuli (pH or temperature change, application of electric or magnetic fields), and share with elastomers some mechanical properties such as elasticity, resilience to stress and endurance to a high number of work cycles. They are good candidates as artificial muscles, since an external stimulus can trigger loss of order within their structure, causing macroscopic shape changes and generation of tension (Figure 1).

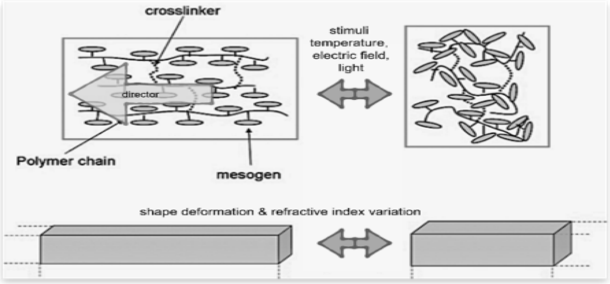

Figure 6. Cartoon representing the shape change
in Liquid Crystalline Elastomersin response to external stimuli.

The presence of azobenzene-based photosensitive groups within their molecular architecture, moreover, enables the use of light to trigger their motion. Light stimulation is desirable, since it guarantees high spatial and temporal accuracy and tunability in terms of power and energy of the source operating the devices (4). Advances and perspectives on the possible biomedical applications of LCEs, mainly as cell scaffolds or as contraction assist devices, will be presented here. The research leading to these results has received funding from Ente Cassa di Risparmio di Firenze (2017/0713).

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WS8 OR13Selective Laser Sintering Fabricated Thermoplastic Polyurethane/Graphene Cellular Structures with Tailorable Properties and High Strain Sensitivity

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Additive manufacturing, also known as 3D printing (3DP), is an innovative manufacturing technology which allows one to turn complex 3D models into real objects without special tooling and with extreme facility, cost, and time savings, alongside high accuracy in the realization of specific complex items. Additionally, 3DP includes several technologies, one if these is the selective laser sintering (SLS). SLS ensures the highest geometrical freedom and dimensional precision. Starting from a computer-aided design (CAD) 3D model, SLS builds up objects by sintering and fusing powder material in a layer-by-layer approach, via a computer-controlled laser. Generally, thermoplastic polymers are mostly used for the laser sintering process. However, only a few polymers are now commercially available. Despite the continuous progress in the optimization of SLS technology, many critical issues still remain unsolved, including the possibility to manufacture multifunctional conductive parts able to exhibit both electrical conductivity alongside lightweight and elastic properties. In this context, it is very interesting to develop new powders made up of conductive nanoparticles dispersed in or coated onto elastomeric particles. Piezoresistive structures, realized by using conductive elastomeric polymers, are commonly used for load/pressure sensors and actuators due to their quick response to external stress. Among them, graphene (GE) has attracted huge interest because of its excellent conductivity, high carrier mobility, optical transparency, and high Young's modulus. The possibility of using TPU powders wrapped with 2D filler as GE, which hinders, to some extent, the coalescence of particles during the sintering, allows for tailoring of the structural and functional properties of the resulting porous structures in a value-range not yet explored. The control of pore morphology and dimension, which depends on the shape of the unit cell, from which the three-dimensional structure is generated, affects their mechanical and electrical response, making them more sensitive to mechanical stress/strain, thus enhancing their stress sensor capability. Herein, the effect of pore morphology and distribution on the thermal, mechanical, and piezoresistive properties of porous structures fabricated by SLS technique by using a home-made powder consisting of TPU wrapped with GE platelets (TPU/GE porous structures) is investigated, specifically, three different geometries have been used, namely Gyroid, Diamond, and Schwarz, with an extent of porosity ranging from 20% to 80%. Electrical and thermal conductivity, mechanical strength, filler dispersion, and interaction with the polymer matrix of the TPU/GE porous structures are investigated and correlated with their porosity and morphology. The reported results are of interest for the design and fabrication of novel 3D printable strain sensors, as well as lightweight thermal conductors.

Simply advanced foams

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Layered and graded foams have proven superior to their uniform counterparts in terms of structural, and functional properties. This is also suggested by nature, abundant with porous material structures whose attributes are far beyond any artificial foam (1). To date, advanced foamed structures are generated via advanced though complex/time consuming technologies (2, 3). Here we explore the possibility to generate layered and graded polymeric foams by using the simple gas foaming technology, with the sole introduction of time-varying boundary conditions of the gas sorption stage (4). We show that, by ingeniously designing the sorption step, it is possible to achieve non-trivial gas concentration profiles and, correspondingly, at pressure release, foams with density and/ or morphology profiles. As a model system, we foamed polystyrene and polycaprolactone with CO_2 and N_2, and achieved three- as well as five-layered foams, gradually or sharply graded, yet in a single foaming step (pressure release) executed after different sorption protocols.

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WS8 OR15

Gold nanoparticles and hyaluronic acid hybrids for enhanced wound healing properties

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The treatment of skin wounds represents an important area of research, due to the central physiological and aesthetic role of this tissue. In recent years, nanoparticles have emerged as important platforms for treating skin wounds. In particular, gold nanoparticles (AuNP), which have specific sizes and shapes and distinctive optical and thermal characteristics, have been demonstrated to exhibit potential therapeutic effects on wound healing (1).

The hyaluronic acid (HA) polymer exists in different lengths, with the different molecular weights that play differently in the various phases of the wound repair. For instance, long and heavy HA chains fill the space with regulatory and structural functions; moreover, in high concentration, they create a porous scaffold network, which allows for the size-selection of cells and proteins, as well as the pathways formation for cell migration (2).

In this work, gold nanoparticles coated with hyaluronic acid (HA-AuNP) were prepared by chemical synthesis and characterized by UV-visible spectroscopy, in order to study the plasmonic properties of hyaluronic acid hybrids with metallic nanoparticles, and their stability during the aging time. Dynamic light scattering (DLS) and atomic force microscopy (AFM) analyses were carried out to characterise the hydrodynamic size and the morphology, respectively. In order to study the interaction of these hybrid polymer-metal nanoparticles with model cell membranes made of supported lipid bilayer, quartz crystal microbalance with Dissipation monitoring (QCM-D) measurements were carried out. The cytotoxicity and ROS production were evaluated on the HUVEC cell line. Furthermore, the way in which these systems influence the wound healing process was examined in parallel by wound scratching assay on the HUVEC cell line and by microbiological studies on pathogenic bacteria strains of *E. Coli* and *S. Aureus*, in order to study respectively their antioxidant and antibacterial synergic effects on the wound healing process.

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WS8 - Poster Communications

- **WS8 PO01 -** C. Amicucci, M. Banchelli, C. D'Andrea, M. de Angelis, F. Cristiano, F. Bertocchi, A. Caneschi, P. Matteini "*Formulation of hybrid nanocomposites based on silver nanowires and graphene derivatives for the fabrication of SERS substrates*"
- **WS8 PO02 -** A. Bellissimo, F. Auriemma, R. Pasquino, N. Grizzuti, C. De Rosa "*Dynamics and structure of Polyvinyl alcohol chains at the interface of two surfaces*"
- **WS8 PO03 -** A. Caneschi, M. Innocenti, M. Briganti, L. Capozzoli, A. Cini, E. Fantechi "*PVD thin films deposited study for applications in the luxury industry*"
- **WS8 PO04 -** A. Cozzolino, N. Baku, P. Rizzo, G. Guerra, Anna Nuzzo, Paolo Vacca "*A New Crystalline Polymer: Poly(2,6-dimethyl-1,4-phenylene)oxide (PPO)*"
- **WS8 PO05 -** M. Gastaldi, A. Fin, N. Barbero, I. Roppolo, A. Chiappone, F. Frascella, S. Bordiga, M. Zanetti, Claudia Barolo "*Innovative functional polymers in the 3D printing*"
- **WS8 PO06 -** T. Mecca, F. Cunsolo, D. Caretti, S. Scurti, M. Ussia, S. C. Carroccio "*New glucamine based highly porous polymers for the adsorption of arsenic from water*"
- **WS8 PO07 -** W. Navarra, O. Sacco, V. Vaiano, C. Daniel, V. Venditto "*Nanocomposite aerogels with photocatalytic properties as smart materials for environmental application*"
- **WS8 PO08 -** F. Rizzi, T. Latronico, A. Panniello, V. Laquintana, N. Denora, I. Arduino, A. Fasano, C. M. Mastroianni, E. Fanizza, M. P. Scavo, M. Striccoli, A. Agostiano, G.M. Liuzzi, M. L. Curri, N. Depalo "*Luminescent PLGA-based nanoparticles as traceable nanocarriers for darunavir brain delivery to treat HIV-associated disorders*"
- **WS8 PO09 -** F. Vischio, N. Depalo, R. M. Iacobazzi, M. P. Scavo, S. Villa, F. Canepa, S. Hee Lee, B. Chul Lee, E. Fanizza, I. Arduino, V. Laquintana, A. Lopalco, A. Lopedota, A. Cutrignelli, M. Striccoli, A. Agostiano, N. Denora, M. L. Curri "*Magnetically targeted delivery of sorafenib through magnetic solid lipid nanoparticles towards treatment of hepatocellular carcinoma*"
- **WS8 PO10 -** M. Milazzo, F. Auriemma, C. De Rosa, D.Capone, R. Pasquino, N. Grizzuti "*Evaluation of curing efficiency of novolac-type phenol-formaldehyde resins for the tuning of multifunctional materials*"
- **WS8 PO11 -** L. Izzo, M. Mella, G. Vigliotta *"How to modulate the inherent antimicrobial activity of thermoplastic polymers based on 2-(Dimethylamino)Ethyl Methacrylate: the role of polymer architecture"*
- **WS8 PO12 -** M. Giorcelli, P. Mandracci, S. Guastella, X. Li, Y. Liang, A. Tagliaferro *"Plasma treatments to improve carbon fibers adhesion on epoxy resin composites"*
- **WS8 PO13 -** S. Cicchi, B. Richichi, M. Mba Blázquez, T. Carofiglio, E. Menna, M. Maggini *"WeGoNANO: multifuctional nanostructured carbon and glycans derivatives for industrial applications"*
- **WS8 PO14 -** L. M. Cucci, S. Kwiek, L. Finocchiaro, I. Pinieri, C. Satriano *"Silica nanoparticles for controlled loading and release of essential oils in multifaceted patches"*
- **WS8 PO15 -** K. Fidecka, D. Williams, I. Yildirim, W. Kamau, S. Mathur, S. Porzio E. Licandro "*Application of academic research on halloysite nanoparticles in the development of BASF's halloysite-based products*"
- **WS8 PO16 -** A. Trusek "*Graphene Oxide as a drug carrier – chemical carrier activation, drug attachment and its enzymatic release*"
- **WS8 PO17 -** B. Oji and M. Sadiq "*Sintering, Characterization and Physical Properties Evaluation of Ceramics Produced From Soda-Lime-Silica Glass and White Corn Cob Ash*"

WS8 PO01

Formulation of hybrid nanocomposites based on silver nanowires and graphene derivatives for the fabrication of SERS substrates

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This work is aimed at finding optimal formulations of silver nanowires (AgNWs) and graphene derivatives, including proper assembly and engineering in 2D substrates, to define a standard, simple and reproducible procedure for surface-enhanced Raman spectroscopy (SERS) detection of genetically modified organisms (GMOs) in the environment. Two hybrid nanocomposites were produced by the combination of AgNWs with two graphene derivatives, *i.e.* graphene oxide (GO) and graphene nanoplatelets (GNP). Each combination was tested upon varying the concentration of the starting materials. Fabrication of the substrates was performed by different protocols according to the peculiar characteristics of GO and GNP: the former was introduced as coating layer over an AgNWs assembly; the latter was used as bulk material in which AgNWs were dispersed. In the first case, the GO layer was obtained by physisorption of GO onto a pre-formed array of AgNWs lying on a PTFE membrane (1). In the second case, a compact GNP sheet containing a random dispersion of AgNWs and with a thickness of tens of micrometers was fabricated. The as-fabricated substrates were analyzed under a microRaman spectrometer to test their optical response. Finally, selected substrates were used for direct detection of GMOs upon simple deposition of few-microliter drops of solution on the top of the substrate followed by evaporation and Raman inspection.

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WS8 PO02

Dynamics and structure of Polyvinyl alcohol chains at the interface of two surfaces

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Polyvinyl alcohol (PVA) is a hydrophilic and biocompatible polymer with excellent film forming properties. As a water-soluble synthetic polymer has found a significant role in many industrial applications including medical patches, artificial skin, coatings, emulsifier and adhesive. In all these applications, PVA is found in solution with solvents that act as plasticizers. In our approach, we focused on the molecular comprehension of polymer-solvent interactions and their diffusion mechanisms to investigate the adhesive properties of PVA.

As water is a good solvent for PVA, water acts as diffusivity enhancer for polymer chains, triggering different processes at the interface. The main role of the solvent is to modify the chain entanglement of PVA. Therefore, the rheology of PVA-water solutions is studied to obtain information about the mobility of PVA, essential for a good interpenetration of chains at the interface, ensuring the adhesion process.

The longest relaxation time of PVA chains, indicative of the mobility of the chains, is evaluated through measurements of viscous (G'') and elastic modulus (G') in typical rheological experiments. The effect of the molecular mass of the PVA and of the concentration of the polymer solution on the longest relaxation time of PVA are analyzed. For the first time we are complementing the Mechanical Rheology with the Diffusing Wave Spectroscopy (DWS). DWS is used to obtain information in a wider spectrum of frequencies, in particular in the high frequency regime, which is prohibitive with a rotational rheometer.

This work has allowed understanding at molecular level diffusive phenomena at the interface of PVA clarifying how the properties and the nature of the polymer/solvent affect the mobility of the chains.

WS8 PO03

PVD thin films deposited study for applications in the luxury industry

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Studies supported by the Regional POR CREO - FESR 2014-2020, project "THIN FASHION" were performed for developing productions alternative to the classic galvanic systems, with the aim to increase the quality of the products and develop a greener process. Moreover, thin films made of various materials are used in many scientific, technological and industrial environments, so progresses in this field will be of interest for several applications. They are deposited through a variety of physical, chemical and electrochemical techniques. In all these fields, it is essential to measure the thickness, the colour, the morphological and compositional of the deposit because the properties of mechanical strength, corrosion, costs, optics and visual appearance depend on this feature.

In this contribution will be described the use of stainless-steel targets and different nitrogen-containing plasma mixtures, allowing to obtain nanostructured coatings consisting of a wide range of single or multiphase layers. Ferritic and austenitic stainless steels were used as targets and different coatings were deposited by magnetron sputtering varying the relative volumetric nitrogen content in the treatment atmosphere. XPS, XRD and electron microscopy analyses were employed to characterize the quality of the obtained samples. Among the result obtained there is the confirm that the incorporation of nitrogen in the film during the reactive plasma process stabilizes and led to lattice expansion of the austenite phase even using a ferritic target. Amongst the various phases produced in SS–N films by reactive sputtering, the S phase is the most interesting since it provides a range of attractive mechanical and corrosion properties, that enhance the quality of the product, one of the targets requested by the luxury brands.

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WS8 PO04

A New Crystalline Polymer: Poly(2,6-dimethyl-1,4-phenylene)oxide (PPO)

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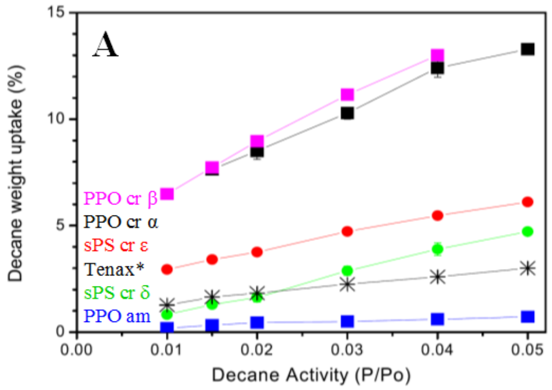
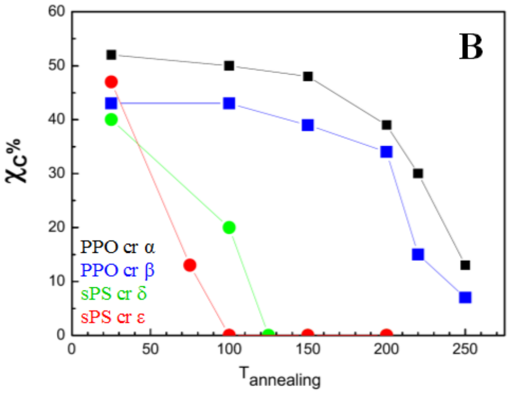
Nanoporous-crystalline (NC) forms have been discovered for two commercial engineering thermoplastics exhibiting several relevant properties, such as a high melting point (> 250 °C), excellent chemical resistance, dimensional stability and low moisture sorption: syndiotactic polystyrene (s-PS) (1) and poly(2,6-dimethyl-1,4-phenylene) oxide (PPO) (2). NC thermoplastic polymers rapidly absorb suitable volatile molecules, even if present in traces in air or water, with high guest selectivity (3), and are promising for applications in chemical separations (4) and molecular sensorics (5). NC polymers present many advantages with respect to nanoporous amorphous polymers as well as with respect to inorganic and organometallic nanoporous materials. Particularly relevant are simple processing conditions (low pressures and temperatures) and automated processing techniques (both from melt and solutions) (6), leading to a large variety of suitable morphologies, like fibers, sheets, films, membranes, foams, gels and aerogels (7). With respect to nanoporous amorphous polymers, NC polymers present the additional advantage of all identical cavities with comparable features to those of NC inorganic and organometallic materials (8).Stereoregular PPO exhibits a high free volume or ultrapermeable amorphous phase so it has been recognized as a membrane material with high permeation parameters, as shown in Figure A (9). Many applications are predictable for PPO NC phases, which present with respect to NC phases of s-PS the advantage of faster guest sorption kinetics, because of the nanoporous nature also of the amorphous phase, as well as the advantage of higher thermal stability, as shown in Figure B (10).





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WS8 PO05

Innovative functional polymers in the 3D printing

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The innovations in the field of technology prompt us to use different methods, not only in prototyping, but also in the production process. One of the most promising technique is the Additive Manufacturing (AM) and, in particular, the 3D printing, which allows to save the raw materials and to realize customizable objects. Among the various printable materials, the plastic ones represent a leading role: thermoplastics are currently printed by fused deposition modelling (FDM) or by selective laser sintering (SLS), while thermoset polymers can be printed exploiting the photopolymerization process in Stereolitography (SL) or digital light processing (DLP) equipment. The exploitation of innovative materials, responsive to external stimuli like light, pH or irradiation at specific wavelengths is one of the most interesting survey (1). The goal is to realize materials that can modulate their properties under external stresses, in a selective and reversible manner.

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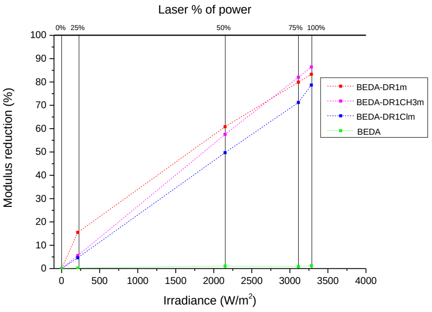

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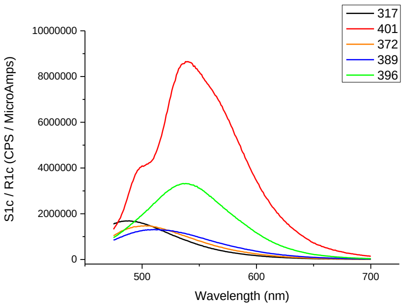

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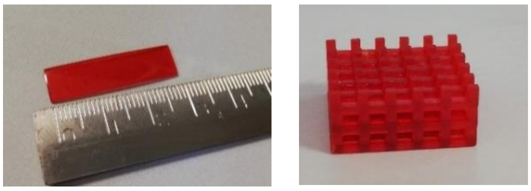

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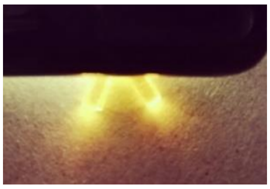

In this work, we have synthesized different functional organic compounds to be use both as dyes, which are a necessary component in the DLP printable formulations, and as functional molecules to obtain printed materials that can show a reduction of elastic modulus under irradiation (Figures 1a, 1b) (2) or a guided emission of light at different wavelengths.

The research leading to these results has received funding from the European Union and the Regione Piemonte (POR FESR/FSE 2014/2020), Piattaforma Tecnologica “Fabbrica Intelligente” – SMART 3D Project.

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WS8 PO06

New glucamine based highly porous polymers for the adsorption of arsenic from water

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Arsenic contamination of drinking water has become as a high priority worldwide problem that affects the health of millions of people. Arsenic compounds are considered as highly toxic substances and their long terms exposure through drinking water causes a severe chronic poisoning. Symptoms of this pathology called *arsenicosis* include skin lesions as hyperpigmentation, hyperkeratosis, as well as cancers in skin, lung, kidney, bladder. (1) Arsenic contamination is worst in Asian countries where it has been reported that 79.9 million people in Bangladesh and 42.7 million in India are exposed to groundwater having above 50 μg/L. (2, 3)

Currently, the maximum arsenic concentration for drinking water is fixed by the World Health Organization (WHO) at 10 μg/L. (4)

Many techniques have been developed to remove arsenic compounds from water, including coagulation-flocculation, membrane filtration, adsorption and ion exchange. (5)

Among various substances developed for the adsorption of arsenic, glucamine based materials have found considerable interest. (6) We have synthesized a new highly porous, glucamine based, polymeric material able to remove arsenic from water with high efficiency. After treatment with this material, the arsenic concentration of a contaminated sample falls far below the permitted limit value for drinking water. Study on efficiency for arsenic removal and selectivity towards other anions will be reported.

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WS8 PO07

Nanocomposite aerogels with photocatalytic properties as smart materials for environmental application

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Nowadays, the water pollution is the most important problem in the world. Typically, to remove water pollutants from wastewater, physical and biological treatment are used. Unfortunately, these treatments can only partially remove the pollutants, without degrading them.
Over the last two decades, an intensive research activity has focused on the study and development of semiconductor photocatalyst nanoparticles (NPs) for the removal of non-biodegradable toxic organic compounds from wastewaters (1). Photocatalyst NPs are particularly efficient for the degradation and mineralization of many recalcitrant organic compounds but their real effectiveness can suffer from particles aggregation in water. Moreover post-treatment recovery from the treated water is a main issue since common photocatalysts such as TiO_2 and ZnO present toxicity both to human and aquatic lives. A possible solution could be to fix the catalyst on supporting organic or inorganic materials (2). Among the considered supports, polymer aerogels are especially appealing as they offer many benefits such as high surface area and high macroscopic operability and recoverability. In addition to these characteristics the photocatalyst aerogels should also maintain high photocatalytic performances associated with high absorption capability for organic compounds as well as good chemical and mechanical stability for a potential large-scale use (3).
In this article the monolithic composite aerogels based on syndiotactic polystyrene (s-PS) and ZnO nanoparticles have been prepared and their photodegradation efficiency has been evaluated using phenol and toluene as water pollutant models. The photocatalyst/s-PS composite aerogels plays a primary role on the photodegradation efficiency, since the polymer acts not only as support for the photocatalyst but also as a pollutant pre-concentrator. The results showed that the synergetic action of s-PS aerogel support (i.e high sorption capacity) and ZnO NPs (i.e. photodegradation of sorbed molecules) makes these composites aerogels particularly efficient to removes organic compounds from water and no decrease of the ZnO photocatalytic efficiency is observed. The high photocatalysis efficiency and complete reusability without regeneration steps of the monolithic ZnO/s-PS composite aerogels associated with the advantages of good chemical stability and excellent mechanical properties allowing an easy recovery after water treatments make these materials extremely interesting for real applications in the removal of organic pollutants from wastewater.

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WS8 PO08

Luminescent PLGA-based Nanoparticles as Traceable Nanocarriers for Darunavir Brain Delivery to Treat HIV-Associated Disorders

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Human Immunodeficiency Virus (HIV)-associated neurocognitive disorders (HAND) are neurological diseases of various severity arising from the invasion of HIV into the central nervous system (CNS). Darunavir (DRV), an antiretroviral drug of the class of HIV protease inhibitors, has been approved for treatment of HIV-infected patients in combination with other antiretroviral drugs. The ability of DRV to inhibit *in vitro* gelatinases A (MMP-2) and B (MMP-9) in astrocytes has been proved. MMP-2 and MMP-9 are two members of the family of matrix metalloproteinases (MMPs), that represent factors responsible for the development of HIV-related neurological disorders.(1) However, owing to its low bioavailability when administered orally, poor water solubility and intermediate CNS penetration effectiveness score, innovative DRV formulation could improve its effectiveness to cross the blood brain barrier (BBB) and ability to reach the targets. The use of optically traceable nanoparticles (NPs) able to encapsulate therapeutic agents may not only enhance drug transport through the BBB and target relevant regions in the brain, but also provide an effective optical monitoring of the process. For this purpose, biodegradable NPs composed of poly (D, L-lactide-co-glycolide) (PLGA) and loaded with biocompatible luminescent Carbon Dots (C-Dots), and DRV were prepared and optically and morphologically investigated. PLGA based NPs offers drug improved stability, high loading capacity, sustained drug release, non-immunogenic property, reduced drug toxicity and enhanced bioavailability, while C-Dots are promising candidate for imaging-guided therapy.(2) The prepared NPs with an average hydrodynamic diameter of ~130 nm, resulted highly stable in aqueous medium, and presented a high drug encapsulation efficiency and emission properties in the visible region. The *in vitro* study on astrocytes demonstrated the high biocompatibility of the NPs and, remarkably, proved their ability to cross BBB (3) in an *in vitro* model and to modulate the expression of MMP-9. The overall results highlight the great promise hold by the luminescent nanoformulations as traceable delivery nanovectors of DRV for the treatment of HAND.

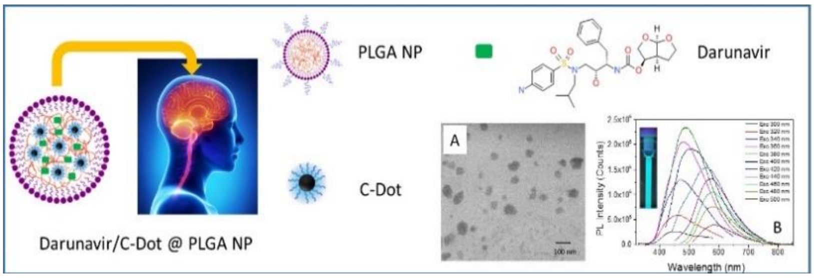

Figure 1: Luminescent PLGA NPs for delivery of DRV to CNS: TEM (A) and PL spectra as a function of excitation wavelength (B) of PLGA NPs loaded with C-Dots and DRV.

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WS8 PO09

Magnetically Targeted Delivery of Sorafenib through Magnetic Solid Lipid Nanoparticles towards Treatment of HepatocellularCarcinoma

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Sorafenib is an anticancer drug with multikinase inhibitor activity and it is only that has proved to significantly prolong the survival time in patients with advanced hepatocellular carcinoma (HCC). However, sorafenib is characterized by severe toxic side effects limiting the possible therapeutic response (1,2). Nanoparticle (NP) based approaches offer a valuable alternative for cancer drug delivery, functioning as a carrier for entry through fenestrations in tumor vasculature, thus allowing direct cell access and ensuring the accumulation of high concentrations of drug to the targeted cancer cell, with a concomitant reduced toxicity of healthy tissue. In this contest, superparamagnetic iron oxide NPs (SPIONs) are very attractive for delivery of therapeutic agents as enhance the drug delivery to specific locations in the body through the application of an external magnetic field (3,4). To make more biocompatible and protect the drug, solid lipid NPs (SLN) has been used to contain sorafenib and SPIONs by means of hot homogenization technique using cetyl palmitate as lipid matrix and polyethylene glycol modified phospholipids (PEG lipids), in order to achieve a PEG-based anti-fouling coating on SLN surface. These nanoformulations, thoroughly investigated by means of complementary techniques, have finally resulted effective drug delivery magnetic nanovectors with good stability in aqueous medium and high drug encapsulation efficiency (>90%). In addition, the magnetic relaxometric characterization has proven that the SLN loaded with sorafenib and SPION are also very efficient contrast agents, with a great potential in magnetic resonance imaging (MRI) technique. Cellular uptake on HepG2 cell line shows a better effectiveness of antitumoral action of sorafenib when it is encapsulated in SLN and subjected to magnetic field. The proposed magnetic SLNs loaded with sorafenib represent promising candidates for image guided and magnetic targeting of sorafenib to liver towards an efficacious treatment of HCC.

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WS8 PO10

Evaluation of curing efficiency of novolac-type phenol-formaldehyde resins for the tuning of multifunctional materials

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Phenolic resin is widely used because it has low cost, good heat resistance, high chemical strength and high mechanical strength (1). The chemical modification and/or the addition of suitable fillers in the system can give desired properties making the material "smart". The curing performance of a homogeneous set of commercial grades of novolac-type phenol formaldehyde (PF) resins is analyzed by using different techniques. They have a statistical (*ortho*/*para*) substitution at aromatic rings and contain from 5 to 15wt% of hexamethylenetetramine (HMTA) as hardener (2). The analyzed grades are modified PF resins, in which the modification consists in the addition of boron/phosphorous compounds, an acrylic rubber, silicone and xylene/phenol copolymer or introduction of aralkyl modifications (3). Their curing behavior is compared with that of an unmodified PF resin in which the cross-linking agent (HMTA) is added into the melted polymer to ensure a good dispersion according to the Hexamine Adduct Phenolic (HAP) technology (1,2). The effect of the different modifications is probed by performing rheological measurements during curing in isothermal conditions. We observe that under similar curing conditions, all modified resins result in a lower stiffness with respect to the unmodified Ph resin obtained by HAP technology. Concerning the curing performance, we introduce two relevant parameters to analyze the data. The first parameter is the "curing ratio". It represents a measure of the efficiency of the functional groups in the resin of generating a three-dimensional network by effect of the heat treatment, already before reaching the isothermal curing step. The second parameter is the "maximum curing rate". It measures how fast, in the early seconds of the isotherm, the partially cross-linked resins transform into a more densely cross-linked network, through the increase of stiffness. Our approach allows identifying the curing performance of the analyzed resins according to four classes. This approach is general, and can be easily extend also to other classes of thermosetting resins. The final mechanical effect of the different modifications is probed by performing dynamical mechanical analysis (DMA). The study of the curing kinetic combined with DMA data allow to understand how to obtain the desired characteristics (e.g. mechanical damping, noise damping, self-healing…) while maintaining the good chemical and mechanical strength properties.

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WS8 PO11

How to Modulate the Inherent Antimicrobial Activity of Thermoplastic Polymers Based on 2-(Dimethylamino)Ethyl Methacrylate: the Role of Polymer Architecture

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The last decades have registered an increasing interest in the development of antimicrobial polymers to prevent the contamination and colonization of materials used in food packaging, textile, water treatment and biomedical application such as medical devices (1). Generally, the strategies used to inhibit growth of microorganisms on surfaces consist either in avoiding microorganisms from attaching or in degrading them. The adhesion resistance involves the functionalization of surfaces principally with poly(ethylene glycol) (PEG) or oligo(ethylene glycol). However, the use of PEG-like materials is limited by its oxidative degradation and the consequent reduction of surface functionality in terms of resistance to protein adsorption. As for degradation, polymers able to deliver antimicrobial agents to the environment have been widely synthesized. However, their capacity to kill bacteria is naturally loosen over time (2). Non-leaching antimicrobial polymeric surface, i.e. with the antimicrobial agent permanently fixed to the surface through covalent bonding, is undoubtedly an attractive alternative strategy to reach the above goals. Most of the literature concerning the preparation of antibacterial surfaces involves the covalent attachment of quaternary ammonium compounds (QAC) by means of an apolar alkyl chain. Here we report the possibility of obtaining thermoplastic polymeric materials containing 2-(dimethylamino)ethyl methacrylate DMAEMA in the structure and overcoming the need for the quaternization process by properly designing the polymeric architecture. The strategy we adopted to obtain the intrinsically antimicrobial material consists in the synthesis of "tree shaped" copolymers with $A(BC)_n$ architecture. "A" is a PEG chain used to both inhibit the protein adhesion avoiding the bacteria proliferation, and produce an hydrophilic environment. "BC" is a copolymeric random chain based on methyl(methacrylate) (MMA) and DMAEMA. The MMA allows the insolubility of materials and represent a sort of chemical spacer between the DMAEMA monomers along the back-bone. We found that these materials show a high antimicrobial activity against Gram positive and negative bacteria, which is switched on in presence of architectures that increase the exposition of cationic groups naturally formed in presence of water. Such a study demonstrated that the key to obtain materials with intrinsically antimicrobial properties copolymerizing non quaternized DMAEMA is the architecture (3).

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WS8 PO12

Plasma treatments to improve carbon fibers adhesion on epoxy resin composites

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Composite materials are becoming one of the main actors in the field of materials for uncountable applications in different fields as aerospace, automotive, sports, etc. In polymer composites the epoxy resin reinforced by carbon fibers is widely used. The performances of epoxy resin/carbon fibres composites are influenced not only by the intrinsic characteristics of the reinforcement (carbon fibers) or by the polymer matrix used (epoxy resin) but also by their physicochemical properties of their interface that affect adhesion. In order to increase polymer fiber adhesions, surface treatments of carbon fibers are required. In this work, derived by MODCOMP EU H2020 Project*, we report results obtained using plasma treatments on carbon fibers to promote the carbon fibers polymer adhesion. Results on surface functionalization using Atmospheric Pressure Plasma (APP), Low Pressure Plasma (LPP) and Active Screen Plasma (APP) are reported. In particular, XPS characterization will be used to demonstrate the creation of functional groups on the carbon fiber surface and FESEM analysis to demonstrate that the carbon fiber surfaces were not damaged.

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WS8 PO13

WeGoNANO: Multifuctional Nanostructured Carbon and Glycans Derivatives for Industrial Applications

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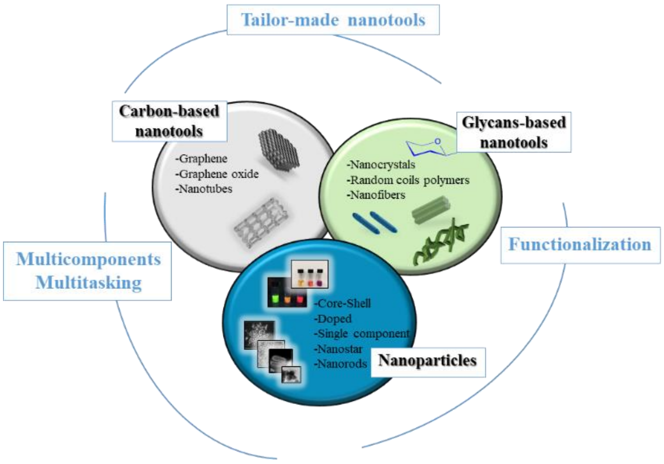
The team of **WeGoNANO** is involved in industrial application driven research activities aimed at developing Carbon and Glycan-based Nanostructured materials. .
The aim of **WeGoNANO** is the preparation of nanomaterials tailor-made for specific needs (*e.g.* preservation to bio-deterioration, barrier to pollutants, conductive plastic materials, catalysis and photocatalysis, biomedical devices)
The workflow moves from the rational design of *ad hoc* nanomaterials to the development of the final product taking into account the *scale up* of the process. This goal will be achieved starting from basic research but bearing in mind the final step: the technology transfer to industrial processes. The main research activity concerns the multi-functionalization of carbon nanotubes, exfoliated graphite, reduced graphene oxide and graphene oxide as well as glycan-based nanocrystals/bio polymers. The materials obtained through these approaches contain graphene and glycans derivatives as platform where a variety of compounds (such as glycans, bioactive molecules, polymeric materials, nanoparticles and dyes) are covalently or supramolecularly linked.



The **WeGoNANO** team possesses expertise and instrumentation to design, synthesize and characterize functionalized nanomaterials and nanocomposites by using classical synthetic approaches in solution as well as mechanochemical synthesis or flow chemistry.

Come and let us know what do you need!!

WS8 PO14

Silica nanoparticles for controlled loading and release of essential oils in multifaceted patches

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Essential oils (EOs) derived from plants are widely used in a variety of applications, including the release of fragrances or active principles in cosmetics, to protect sensitive ingredients against oxidative processes and environmental aggressions (e.g. light, moisture, bacteria) in food and pharmaceutical industries, as well as antimicrobial and repellent agents in topical applications (1, 2). Although their promising property, the labile and volatile nature of EOs reduces their activity during application or storage and requires repeated application after times for achieving a long-time efficacy. An attractive strategy derived from the encapsulation of EOs into nano-delivery systems which protect the natural essences from environmental influence and allow for a controlled release of the entrapped molecules.

Nanocarriers, indeed, acting as barriers between the included molecules and the environment, are able to reduce evaporation, photodegradation, and physicochemical stress of EOs (3). In this work, essential oils were encapsulated into chemically stable and porous silica nanoparticles (SiO_2-NPs), thus permitting a controlled release of their volatile constituents (4).

The high encapsulation efficiency, the long-term stability and the EOs release profile were investigated by means of UV-visible and fluorescence spectroscopy. The oil loading into the porous structure of SiO_2-NPs as well as the morphology and the hydrodynamic size of the synthesized nano-systems was assessed by AFM and DLS measures. Cell viability assay on human dermal fibroblasts (HFF1) confirms the low cytotoxicity of the studied nanosystems. The optimized formulations were, subsequently, entrapped into polymeric patches for topical applications and fluorescence spectroscopy provides evidences of the long-term release of the EOs.

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WS8 PO15

Application of academic research on halloysite nanoparticles in the development of BASF's halloysite-based products

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BASF worldwide reinforcement in major markets of chemical industry, has led the company to look for innovative products, to come out to customers with intelligent solutions and to welcome changes as incoming opportunities. Bearing that in mind, Northern America Group of BASF company has directed its attention to the smart use of innovative nanotechnology that could eventually enhance performance of its offered kaolin-based products. Therefore, it has been decided to explore the potential of halloysite nanotubes (HNTs) in the development of various BASF's industrial products, such as paints, coatings, plastics and ceramic honeycombs catalysts. This quite unknown nevertheless triggering attention nanoparticle, is being noticed as a high-performance mineral additive, embracing various product's properties, such as optical and mechanical ones (1). Specifically, the addition of halloysite clay is associated with enhancement of product's brightness, whiteness and opacity. Furthermore, application of halloysite improves products' mechanical strength, reduces thermal expansion and increases their porosity. Nevertheless, the use of halloysite contributes to low-cost and sustainable development, since it is a cheap, natural and environmentally friendly nanoparticle (2). Despite above-described benefits of halloysite implementation in the industrial products manufacturing, preliminary experimental trials have shown several difficulties during halloysite manipulation. Sample's dispersion, as well as the removal of significant amount of iron impurities from HNT's bulk sample, appeared to be difficult to achieve. Scientifically challenging is also the removal of moisture (~ 2%) from the pristine HNT's bulk samples. In this regard, overcoming above-raised unfavorable aspects could promise successful halloysite-based products' preparation and the enlargement of the halloysite market. In order to provide scientific solutions for raised difficulties, as well as to increase the knowledge in newly developing halloysite's field, BASF has established a co-beneficial collaboration with an international research group specialized in halloysite nanotechnology, the group of Professor Emanuela Licandro (University of Milan, Italy). The common goal was to bridge the fundamental research on halloysite in academia with addressed needs of the industry. Therefore, we present the joint study focused on performance validation and properties enhancement of halloysite-based products, that could be further potentially manufacturable in BASF company on an industrial scale. The communication is dedicated to one of the studied aspects, which is the pH-dependent dispersion behavior of halloysite nanotubes. This will impact the percentage of present aggregates, the low shear viscosity and the solids' loading capacity in final halloysite-based products. The obtained results are completed with the physicochemical characterization, such as ζ-potential, Microtrac size analysis and kinetics of sedimentation study that allowed to rationalize the case study. In conclusion, the conducted research stands out as an example of an efficient collaboration to achieve a shared goal: the simultaneous extensive knowledge of academia and the continuous search for world-leading resources of the industry.

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WS8 PO16

Graphene Oxide as a Drug Carrier – Chemical Carrier Activation, Drug Attachment and Its Enzymatic Release

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Graphene oxide (GO), due to its properties, such as nanometric dimensions, large specific surface area and good biocompatibility, can be used as a carrier in controlled drug release systems. The surface of graphene is easily functionalized. Carbon atoms on the graphene plane are characterized by sp2 type hybridization, which affects the strong covalent bonds between them and the current delocalization of π electrons. During the interaction of the graphene plane with foreign molecules or atoms, the π-π coupling is modified, which results in a change in density distribution and thus in the chemical and physical properties of the material. Two methods of graphene functionalization are known, covalent and non-covalent methods (1). Covalent functionalization of the graphene surface is associated with a change in the degree of hybridization of carbon atoms building this structure from sp2 to sp3. The process of graphene functionalization using the oxidation process leads to the formation of GO. The hydroxyl and carboxyl groups present on the GO surface after their prior activation, are capable of creating covalent bonds. Activation can occur through different activators and then different compounds can by attached to carrier (2). The procedure of GO chemical activation before drug molecules bound was elaborated. Doxorubicin (DOX), an anticancer drug, was attached to the surface of GO via the Gly-Gly-Leu linker. Approximatelly $3.07 \cdot 10^{20}$ molecules of the tripeptide were attached to 1 gram of GO and then almost the same number of DOX molecules. The bound DOX was effectively released using thermolysin, an enzyme cleaving peptide bonds between Gly and Leu inside the linker structure. The thermolysin, in its native form was immobilized inside a core-shell carrier. A porous membrane as the shell was responsible for keeping enzyme molecules and GO particles inside the carrier, simultaneously allowing for the released drug molecules through diffusion outside. The proposed type of core-shell drug carrier based on GO, for which the rate of drug release is controlled by the enzyme concentration delivered with the carrier is a completely novel solution. The limitation of this type of drug carrier is the necessary presence of the reactive group in the drug molecule and the use of an enzyme that will remain active throughout the therapy. It was possible to bond DOX to GO with satisfactory efficiency, but impossible to release the whole mass of attached DOX. The third stage of enzymatic hydrolysis was very slow.

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WS8 PO17

Sintering, Characterization and Physical Properties Evaluation of Ceramics Produced From Soda-Lime-Silica Glass and White Corn Cob Ash

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This research examines the influence of soda-lime-silica glass on the porosity, crystallization behavior and phase transformation of ceramics produced from white corn cob ash. The waste soda lime glass (SLG) was crushed and sieved into grain sizes of 45µm using a metallurgical sieve operated via a sieve shaker machine operated for 15minutes. The corn cob (CCA) was ash and conditioned at a temperature of 700^0C for 6hrs in a muffle furnace before been screened. A mixture of 98, 96, 94, and 92% of CCA and 2, 4, 6, 8% of SLG were mixed in a ball mill and formed into pellets using polyvinyl alcohol (PVA) as binder and then sintered at temperatures of 900^0C, 1000^0C and 1200^0C respectively. Microstructure analysis (SEM), XRD, XRF and FTIR analysis were used to determine the porosity, crystallization behavior, elemental composition and chemical bond formed in the developed ceramics material. Archimedes and geometric measurement were also employed to determine the bulk density and linear shrinkage of the material. The SEM image showed that as the sintering temperature increases, the porosity of the formed ceramics decreases. The XRD reveals the crystallization behavior of the produced samples after firing with a cristobalite dominant phase and small traces of tridymite phase noted in the samples. Fourier transform infrared spectroscope (FTIR) was used to analyze the chemical bond formed in the material.

Keywords: Microstructure analysis, Corn Cob Ash, Phase transformation, sintering temperature, Crystallization