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REALIZING CIAMICIAN'S ENERGY FUTURE

Giacomo Ciamician imagined a future sustained only by sunlight, air and water - the Artificial Leaf and Bionic Leaf enable such a future. The Artificial Leaf uses sunlight to split H_2O to H_2 and O_2. The Bionic Leaf-C takes the H_2 from the catalysts of the Artificial Leaf and combines it with CO_2 in air to make biomass and liquid fuels at efficiencies that are 10 to 100 times greater than natural photosynthesis. Extending the approach, the Bionic Leaf-N combines the H_2 from the Artificial Leaf with N_2 in the air to make a sustainable fertilizer. These discoveries of distributed Fischer-Tropsch and Haber-Bosch processes are particularly useful to the underserved of the world, where large infrastructures for fuel and food production do not exist.

Giacomo Ciamician was the world's first solar photochemist. Photographs show Ciamician walking among flasks and beakers exposed to the rays of sunlight on the roof of the University of Bologna. An observed physical or chemical change in a flask or beaker indicated to Ciamician a solar photoreaction deserving of study. With this deep appreciation of the power and utility of the sun, Ciamician wrote an article for *Science* in 1912 entitled "The Photochemistry of the Future" that was stunning in its vision [1]. Ciamician identifies fossil fuels (in his day, coal) as an exhaustible natural resource and urges for new research that will lead to the discovery of solar-driven processes. With uncanny prescience, Ciamician proposes the concepts of biomass conversion ("the cultivation of plants may be so regulated as to make them produce abundantly such substances as can become sources of energy"), biotechnology ("through suitable inoculations" to obtain products "from plants that usually do not produce them"), N_2 and CO_2 fixation ("by using suitable catalyzers"), photovoltaics ("it is conceivable that we might make photoelectrical batteries or batteries based on photochemical processes") and a number of potential light-based technologies. He then poses his most compelling challenge - mastery of "the photochemical processes that hitherto have been the guarded secret of the plants" with the goal of using the sun to replace fossil-derived energy sources.

A response to Ciamician's prescient challenge is now needed more than ever. Energy demand by

The award ***"Premio Città di Firenze sulle Scienze Molecolari"*** **was established in 2002 from an idea born at the Scientific Pole of the University of Florence and in particular at the Magnetic Resonance Center (CERM) by initiative of the late Prof. Ivano Bertini. It is intended as a tribute of the City of Florence to the scientific community and to the commitment of the researchers to improve the future of mankind.**
It is an occasion to solicit for the interest of the civic society on the importance of the scientific research for the development of the Country and to the benefit of mankind.
The award is assigned to outstanding molecular scientists in recognition of their contribution to the scientific progress. The winners of the past editions are all prominent figures in their research field, ranging from biophysics, to energy, from molecular genomics to the most modern applications of chemical research in pharmacology, diagnostics and therapeutics.
More info: https://www.cerm.unifi.it/premio-citta-di-firenze

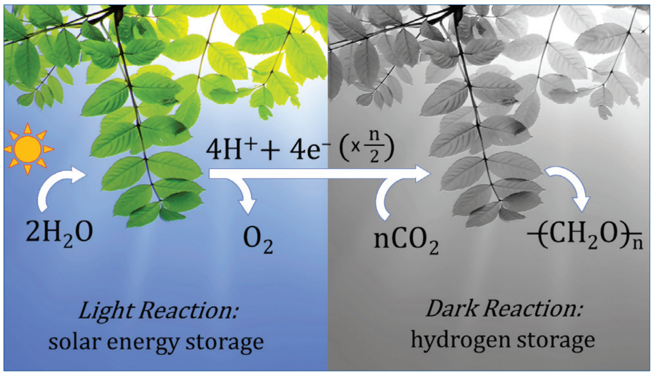

Fig. 1 - Photosynthesis proceeds by light and dark reactions. In the light reaction, solar photons are stored by rearranging the bonds of water to hydrogen and oxygen. In the dark reaction, the hydrogen produced from water splitting is stored by fixing it with carbon dioxide to produce biomass and carbohydrates

mid-century will be driven by 3 billion people currently without access to reliable energy and 3 billion new inhabitants to our planet who will primarily reside in the Global South. With the understanding that climate change will largely be driven by these 6 billion new energy users, providing this cohort with carbon neutral energy is a requisite to mitigating climate change. To achieve this goal, a new science needs to be discovered - the science envisioned by Ciamician. Mastery of the photosynthetic process furnishes a distributed and renewable energy system that uses sustainable inputs - sunlight, air and water - that are available to all.

This article, summarizing a lecture delivered on the occasion of the "Premio Città di Firenze", describes science advances that meet Ciamician's challenge from over a century ago. The Artificial Leaf and Bionic Leaf enable distributed and renewable systems for biomass, fuels, and fertilizer production, and the synthesis of complex molecules such as vitamins using the inputs of only sunlight, air and any water source.

Natural Photosynthesis

Photosynthesis comprises light and dark processes (Fig. 1). In the light process, the leaf absorbs solar light to rearrange the bonds of H_2O to O_2 and "H_2", which is fixed as NADPH/H^+ in Nature. In the dark process, the "H_2" is combined with CO_2 to produce biomass and/or carbohydrate. Thus, in photosynthesis, energy storage of solar light is achieved by water splitting whereas the production of carbohydrate/biomass is Nature's method of storing the H_2 that is released from water-splitting reaction. As shown in Fig. 1, the water-splitting light reaction is a 4-electron/4-proton reaction and the carbon-fixing dark reactions involve a multiple ne$^-$/nH$^+$ (*e.g.*, n = 24 for glucose, $C_6H_{12}O_6$) reaction. Consequently, in heeding Ciamician's call to master photosynthesis, we set out on three major paths:

1) the creation of an experimental and theoretical framework to describe the coupling of electrons to protons;
2) the creation of the Artificial Leaf to accomplish the light reaction of photosynthesis, *i.e.*, the splitting of H_2O to O_2 and H_2;
3) the creation of the Bionic Leaf to accomplish the dark reaction, by taking the H_2 produced from the catalysts of the Artificial Leaf and combining it with CO_2 to produce biomass and liquid fuels.

Proton-Coupled Electron Transfer

The coupling of electrons to protons in the light and dark reactions of photosynthesis is needed for high energy efficiency [2]. When we began our studies, a framework for proton-coupled electron transfer (PCET) did not exist, leading us to design the first experiments to temporally resolve the movement of an electron coupled to a proton [3-5]. These

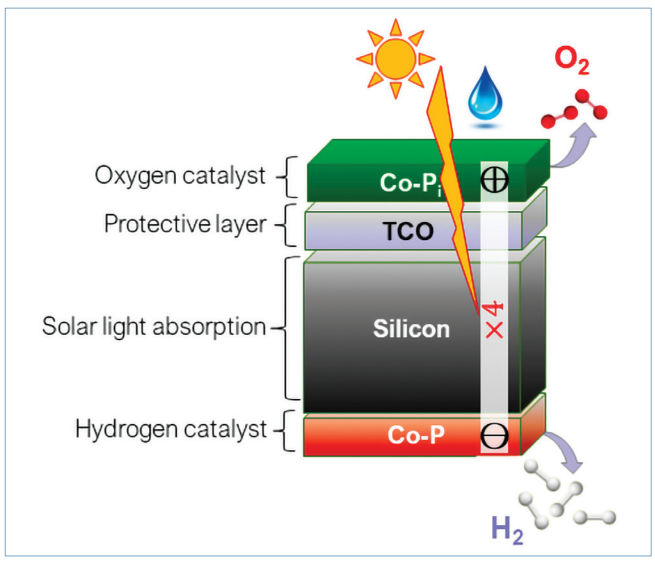

Fig. 2 - The Artificial Leaf: the p-side of Si is coated with protective transparent conducting oxide (TCO) and CoPi OER catalyst layers. The n-side is coated with a Co-P HER catalyst layer. Similar to the Kok cycle in the Photosystem, the absorption of four photons produces the oxidizing and reducing equivalents for water splitting

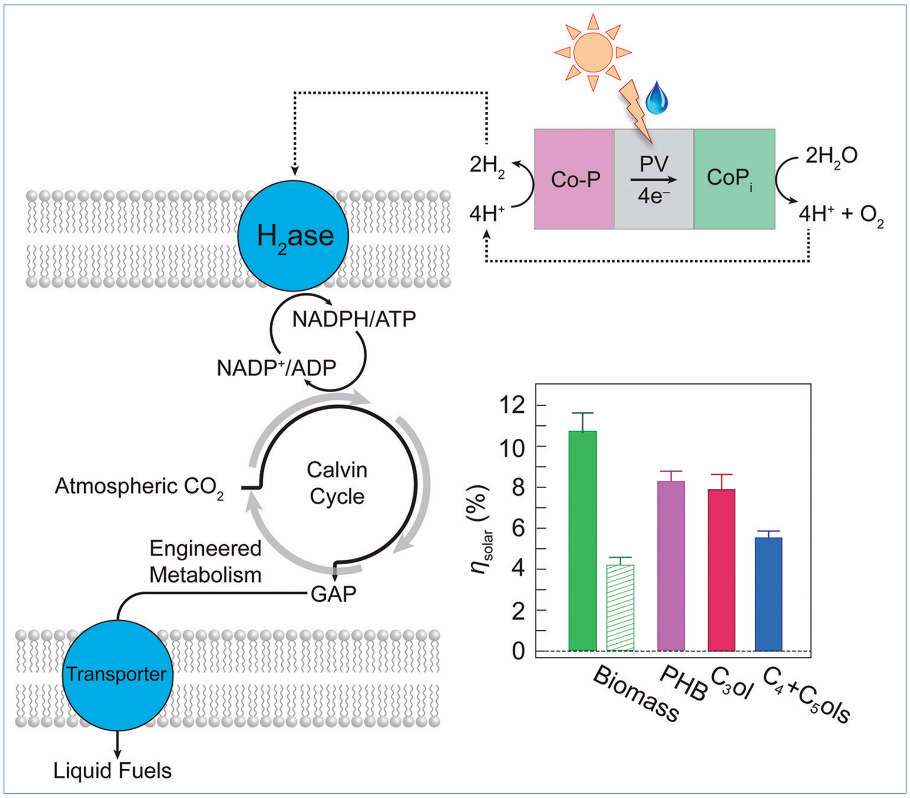

Fig. 3 - Bionic Leaf-**C**: H_2 produced from the catalysts of the Artificial Leaf is used to power cellular biomachinery of the bacteria, *C. necator*, for CO_2 fixation to produce biomass or liquid fuels along engineered metabolic pathways. The inset shows the solar energy efficiencies, driven by a photovoltaic device of 20% efficiency for: biomass = *C. necator* and PHB = polyhydroxybutyrate; C_3ol = isopropanol; and C_4+C_5ols (isobutanol + isopentanol)

experimental kinetics measurements provided a framework in which we developed the first theory for PCET **[6]**. Upon this foundation of PCET, cobalt/nickel-phosphate/borate (Co/Ni-P_i/B_i) oxygen evolution reaction (OER) catalysts **[7, 8]** and NiMoZn and Co-P hydrogen evolution reaction (HER) catalysts were developed. These catalysts are unique because they are self-healing **[9, 10]** and continually renew themselves during OER. The ability to perform water splitting under mild conditions as a result of self-healing has the advantages of (i) using any water source (*e.g.*, seawater, natural water, wastewater **[11, 12]**), (ii) facilitating the interfacing of water-splitting catalysts with materials such as Si, and (iii) operating in buffered water, thus allowing for the integration of water-splitting catalysts with microorganisms.

The Artificial Leaf

The Artificial Leaf accomplishes the light reaction of photosynthesis. It is composed of a silicon wafer coated on one side with the CoP_i or NiB_i OER catalyst and the other side with a NiMoZn or a cobalt-phosphide (Co-P) HER catalyst **[13]** (Fig. 2). The ability to perform water splitting at pH 7 allows for Si corrosion to be easily avoided by protecting it with a simple transparent conducting oxide (TCO). The Artificial Leaf is the first wireless water-splitting device, capturing the light reaction of photosynthesis - the use of sunlight to split H_2O to H_2 and O_2 from neutral water at atmospheric pressure and room temperature but at water-splitting efficiencies that are much greater than Photosystems II and I **[14]**. Moreover, the Artificial Leaf achieves an important milestone with regard to storing solar energy for the underserved as it is a minimally engineered device (Si with simple coatings) that can operate from locally sourced water.

The Bionic Leaf-C

The Bionic Leaf-**C** accomplishes the dark reaction of photosynthesis **[15, 16]**. It uses the H_2 generated by the catalysts of the Artificial Leaf to power the cellular biosynthetic machinery of a bacterial microorganism, *C. necator*, to convert carbon dioxide from air into biomass and liquid fuels. The H_2 from water splitting is coupled to the production of NADPH and ATP within the cell *via* hydrogenases; ATP (cellular energy source) and the NADPH (reducing source) in turn drive the fixation of carbon dioxide from air (Fig. 3). As shown in the inset, a solar-to-biomass yield of 10.8% is achieved using a 20% photovoltaic device. This biomass efficiency accounts for H_2 generation, H_2 solubility, and the energy efficiency associated with cell growth and maintenance. Moreover, the Bionic Leaf-**C** operating in air (hatched line in inset bar graph) is only 2.7 times lower in efficiency than that when it operates in pure CO_2, despite a CO_2 concentration difference between air and pure CO_2 of 2500, demonstrating the effectiveness of carbon-concen-

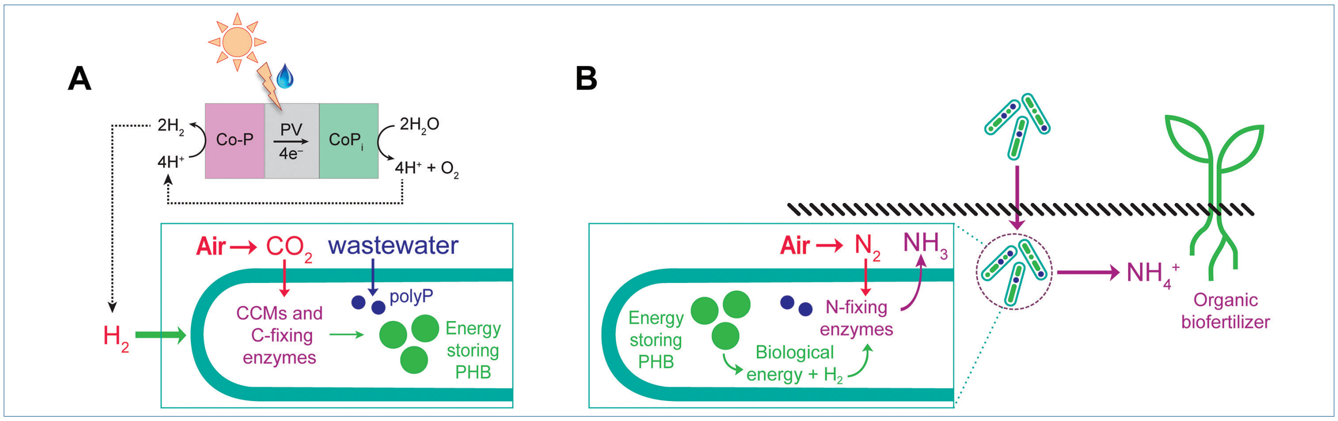

Fig. 4 - The Bionic Leaf-**N**: A) The bacteria *Xanthobacter autotrophicus (X.a.)* combines H_2 from solar water splitting with CO_2 to produce polyhydroxybutyrate (PHB) and then (B) draws on the PHB as internal energy and hydrogen supply to power the nitrogen fixation cycle to produce ammonia and solid N biomass. Once PHB is produced, a solar source is no longer needed as solar light is effectivelty stored in PHB. The organism may then be introduced into soil to fix nitrogen for crop fertilization. When grown in the presence of wastewater, the organism will also sequester P in the form of cyclic and linear polyphosphate (polyP). The process allows for the sustainable and distributed production of fertilizer from sunlight, atmospheric CO_2 and N_2 and wastewater

trating mechanisms in the microorganism. The carbon flux within the Bionic Leaf-**C** may be redirected from cell growth (*i.e.*, biomass) to metabolically engineered pathways placed in the microorganism to result in the synthesis of liquid alcohols, namely isopropanol (C_3), isobutanol (C_4) and isopentanol (C_5) at solar-to-liquid fuel efficiencies of 6 to 8%, depending on the liquid fuel. Thus, the Bionic Leaf-**C** is x10 more efficient than natural photosynthesis for the best growing biomass (*e.g.*, 1% for soy, switch grass), and with regard to liquid fuels, is x100 times more efficient than the best biomass-to-biofuels processes. In effect, the Bionic Leaf-**C** is a distributed and sustainable surrogate for Fischer-Tropsch using only sunlight, air and water as its inputs.

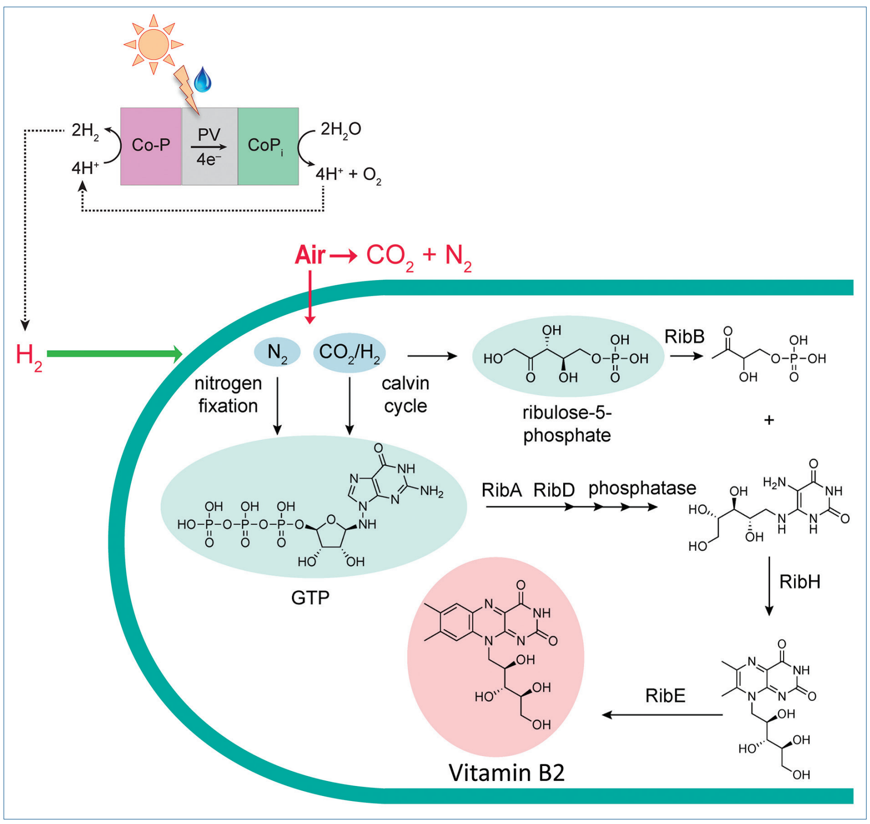

Fig. 5 - Bionic Leaf-**N** for sustainable chemical synthesis.
Vitamin B2 produced from sunlight, air and water by an engineered *X.a.*

The Bionic Leaf-N and Sustainable Manufacturing

The Bionic Leaf-**N** is an extension of the Bionic Leaf-**C** and is able to fix carbon dioxide and nitrogen from air **[17]**. A microorganism, *Xanthobacter autotrophicus (X.a.)* has parallel C- and N-fixing pathways (Fig. 4). The C-fixing pathway operates in a similar fashion to the Bionic Leaf-**C**; H_2 produced from the catalysts of the Artificial Leaf is combined with CO_2 from air to produce polyhydroxybutyrate (PHB), which is stored internally within *X.a.* The PHB biopolymer provides the bacteria with an energy supply, as it is a nascent source of intracellular energy (ATP) and hydrogen (NADPH/H+). With its own internal energy, *X.a.*-

PHB fixes nitrogen at exceptionally high turnover frequency (1.9x10^4 s^{-1} per bacterial cell) and turnover number (9x10^9 bacterial $cell^{-1}$). The Bionic Leaf-**N** as a living biofertilizer is consequential to mitigating CO_2 release into the atmosphere, as the industrial synthesis of ammonia results in CO_2 emissions that are greater than for any other chemical-making reaction **[18]**. As an example, in a large 400-acre farm trial for leafy vegetables, 130 lbs of N was needed per acre for crop growth. By replacing 90% of the chemical fertilizer with the Bionic Leaf-**N**, 153 metric tons of carbon dioxide was prevented from being released into the atmosphere **[2]**. Additionally, the Bionic Leaf-**N** is important to sustainable farming as it avoids nitrogen runoff, as well as fixing P from wastewater **[19]** to allow for the cycling of the biogenic elements of C, N and P.

Beyond fertilizer production, the powerful tool of synthetic biology allows the Bionic Leaf-**C/N** to be generalized as a renewable chemicals synthesis platform, depending on the biomachinery to which water splitting is coupled. As an example of the power of the approach, we have metabolically engineered *X.a.* to fix carbon and nitrogen from air to produce the complex heterocycle, vitamin B2 (Fig. 5), if you will, vitamins from thin air **[20]**.

Concluding Comment

With the discovery of PCET, the Artificial Leaf and the Bionic Leaf, we find satisfaction in contributing to future generations the consoling prophecy of Ciamician "…if our black and nervous civilization, based on coal, shall be followed by a quieter civilization based on the utilization of solar energy, that will not be harmful to progress and to human happiness".

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Realizzare il futuro energetico di Ciamician

La foglia artificiale e la foglia bionica permetterebbero di realizzare il sogno di Giacomo Ciamician, che immaginava un futuro energetico basato solo su luce solare, aria e acqua. La foglia artificiale utilizza la luce solare per scindere l'acqua in idrogeno e ossigeno. La Bionic Leaf-C prende l'idrogeno prodotto grazie ai catalizzatori attivi nella foglia artificiale e lo combina con la CO_2 presente nell'aria per produrre biomassa e combustibili liquidi con efficienze da 10 a 100 volte superiori alla fotosintesi naturale. Analogamente, la Bionic Leaf-N combina l'idrogeno della foglia artificiale con l'azoto presente nell'aria per creare un fertilizzante sostenibile. Queste scoperte, derivate dai processi Fischer-Tropsch e Haber-Bosch, sono particolarmente utili per le popolazioni dove non esistono grandi infrastrutture per la produzione di carburante e cibo.