SUSTAINABLE ENERGY PRODUCTION AND MANUFACTURING USING ONLY SUNLIGHT, AIR AND WATER

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Energy demand in the 21st century will roughly double by mid-century owing to rising living standards in emerging economies and to a growing world population, primarily located in the Global South. Most of the increased demand will come from 3 billion people currently without access to reliable energy and 3 billion new inhabitants to our planet who will mostly reside in the Global South. For this reason, this global cohort will have a major impact on climate change over the approaching decades. Providing these 6 billion people with carbon neutral alternatives to meet their societal energy needs is a requisite to mitigating climate change. To meet the increased energy demand of these 6 billion additional energy users will require invention, development and deployment of carbon-neutral energy and energy-intensive processes on a scale commensurate with, or larger than, the entire present-day energy supply from all sources combined.

Nowhere has science wandered away more from the world it needs to serve most than in the field of energy. Addressing the energy needs of the underserved requires us to rethink how energy systems are implemented. Energy systems of today are heavily engineered, and they are designed to rely on a centralized infrastructure. In addressing the underserved, the dogma is to translate science discoveries and attendant technologies that have worked in the developed world to the emerging world (i.e., pound the square peg into the round hole). However, climate change is outpacing the accrual of wealth needed to realize centralized infrastructures in the developing world. A new science needs to be discovered. Critical to this rethinking is a move towards a more low-cost and distributed energy ecosystem where both the production and delivery of energy is better aligned with the context of the underdeveloped regions of the world. Specifically, what new science will engender distributed energy systems that uses sustainable inputs that are available to all? We have addressed this question with a series of science advances that underpin distributed and sustainable systems for biomass, fuels, and fertilizer production, and the synthesis of complex molecules such as vitamins using the inputs of only solar energy, air and any water source.

Self-Healing Catalysis: Solar Water Splitting Using Any Water Source

All sustainable energy conversion schemes eventually rely on water as the source for proton and electron reducing equivalents. Because the coupling of the electron and proton is demanded for high energy efficiency, we were led to create the field of proton coupled electron transfer (PCET) at a mechanistic level [1] with the first measurements that temporally resolved the movement of an electron coupled to a proton, followed by the development of the first theory of PCET [2]. Controlling PCET is at the heart of efficiently harnessing the protons and electrons of the water splitting reaction, in which the energy of a solar light input is stored in the rearranged bonds of two water molecules to produce hydrogen (×2, $4H^+/4e^-$) and oxygen [3].

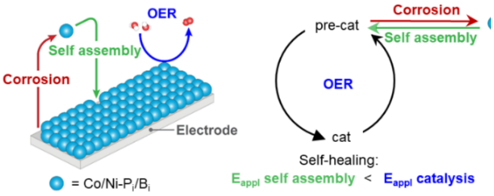

Fig. 1. Self-healing OER Catalysis. Self-healing is achieved if the potential for self-assembly of the Co/Ni-P_i/B_i OER catalyst (blue spheres) is less than the potential for water splitting.

The implementation of water splitting for distributed energy systems in the developing world presents major challenges and thus an imperative for new science. Foremost is the criterion to develop catalysts that operate in any water source. Most water splitting catalysts require concentrated base where the protons that are released from the oxygen evolution reaction (OER) are readily neutralized. In natural waters, however, the concentration of hydroxide is small and the strongest base is the oxide, which readily reacts with acid, thus leading to its corrosion by its dissolution. To overcome corrosion, we developed cobalt/nickel-phosphate/borate (Co/Ni-P_i/B_i) catalysts [4,5] that are self-healing [6,7] wherein an equilibrium for catalyst self-assembly is established that lies energetically within that for the oxygen evolution reaction (OER) of water splitting catalysis (Fig. 1). Because these self-healing catalysts continually renew themselves during OER, they can operate in neutral and natural waters, including wastewater [8,9]. The ability to perform OER under neutral conditions has several advantages. Firstly, a major milestone is achieved with regard to responding to the underserved as solar water splitting is not reliant on a specific water source and it may be found locally. Secondly, the catalysts operating under mild environmental conditions facilitates their interface with materials such as Si, which is unstable in corrosive basic conditions. Finally, the ability to operate water splitting from buffered water allows for the integration of water splitting catalysis with bioorganisms.

Artificial Leaf: Emulating the Solar Energy Reaction of Photosynthesis

The ability to interface water splitting catalysts with Si under non-corrosive conditions led to the development of the Artificial Leaf [10,11]. The Artificial Leaf, which is the first wireless water splitting device, comprises a silicon wafer coated on one side with the Co-P_i OER catalyst and the other side with a NiMoZn alloy or a cobalt-phosphide (Co-P) hydrogen evolution reaction (HER) catalyst (Fig. 2). The Artificial Leaf is quite remarkable. When immersed in any water source and exposed to sunlight, oxygen bubbles from the OER side of the wafer and hydrogen bubbles from the HER side of the wafer at a rate that is commensurate with the solar flux impinging on the silicon. The Artificial Leaf captures the direct solar process of photosynthesis – the use of sunlight to split water to hydrogen and oxygen from neutral water, at atmospheric pressure and room temperature. However, inorganic water splitting systems such as the Artificial Leaf can absorb light and separate charge at efficiencies [12] much greater than Photosystems II and I [13] (PSII and PSI, respectively) and hence solar-to-fuels (hydrogen-oxygen) efficiencies are much greater than that achieved by the photosynthetic membrane for water splitting. Here again, the Artificial Leaf achieves an important milestone with regard to the undeserved—a minimally engineered device, Si with simple coatings, can produce oxygen and hydrogen from natural water and wastewater sources with sunlight as an input.

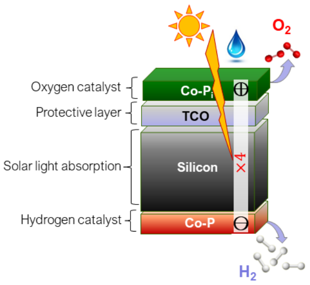

Fig. 2. The Artificial Leaf. The p-side of a Si is coated with a transparent conducting oxide (TCO) protective layer and a Co-P_i OER catalyst. The n-side is coated with a Co-P HER catalyst. Similar to the Kok cycle in Photosystem II, the absorption of four photons to produce oxidizing and reducing equivalents are translated into energy storge via the water splitting reaction using natural- or waste- water.

Bionic Leaf-C: Distributed Carbon Fixation to Biomass and Fuels

The Bionic Leaf-**C** was created to use the hydrogen produced from the catalysts of the Artificial Leaf to power the cellular biosynthetic machinery of bacterial microorganisms to convert carbon dioxide from air into biomass and liquid fuels [14]. In this approach, the entire PSI and PSII water splitting assembly of the photosynthetic membrane is replaced by catalysts of the Artificial Leaf. The hydrogen from water splitting is coupled to the production of NADPH within the cell via hydrogenases; the NADPH in turn drives cellular energy production (ATP) and is also the reductant for the fixation of carbon dioxide from air (Fig. 3). A solar-to-biomass yield of 10.8% is achieved with a typical Si photovoltaic efficiency of 20%. The over biomass efficiency is authentic as it accounts for limitations arising from H_2 generation from water splitting, H_2 solubility, and the energy efficiency associated with biomass maintenance and growth. Moreover, Bionic Leaf-**C** operating in air is only 2.7 times lower in efficiency than that when it operates in pure CO_2, despite a CO_2 concentration

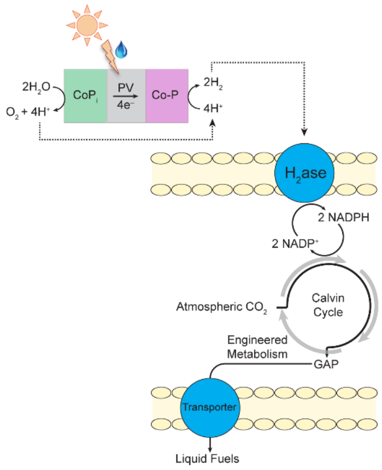

Fig. 3. Bionic Leaf-**C**. H_2 produced from the catalysts of the Artificial Leaf is used to power cellular biomachinery for CO_2 fixation along engineered metabolic pathways to make liquid fuels.

difference between air and pure CO_2 of 2500. The high product yield for the Bionic Leaf-**C** in air demonstrates the advantages offered by biological carbon-concentrating mechanisms to alleviate mass transport limitations, absorb solubilized CO_2 and maintain high intracellular CO_2 concentrations. The carbon flux within the Bionic Leaf-**C** may be redirected from cell growth (i.e., biomass) to metabolically engineered pathways placed in the bioorganism 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 ten times more efficient than natural photosynthesis for the best growing biomass (e.g., 1% for soy, switch grass) [15], and with regard to liquid fuels, is 50 to 100 times more efficient than that provided from natural biomass. The Bionic Leaf-C in effect is a distributed and sustainable surrogate for Fischer-Tropsch using only air, water and sunlight as its inputs.

Bionic Leaf-N: Distributed Nitrogen Fixation to Fertilizer

Extending the hybrid inorganic-biological (HIB) approach, we have realized a renewable and distributed Haber-Bosch process with the creation of the Bionic Leaf-**N** [16]. The Bionic Leaf-**N** uses the autotropic and nitrogen fixing microorganism, *Xanthobacter autotrophicus* (*X.a.*), which has parallel C- and N- fixing pathways and may be directly grown from hydrogen (Fig. 4). *X.a.*, as all nitrogen-fixing bioorganisms, down regulates nitrogen fixation owing to the enormous energy intensity required to convert nitrogen to ammonia (nitrogenase requires 16 ATPs per nitrogen molecule). To overcome this roadblock, we have combined the hydrogen produced from the catalysts of the Artificial Leaf with CO_2 from air to produce polyhydroxybutyrate (PHB), which is stored internally within the bacteria. 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 and hydrogen supplies, down regulation of nitrogen fixation in *X.a.*-PHB is mitigated and nitrogen fixation in the form of ammonia and "N" biomass occurs

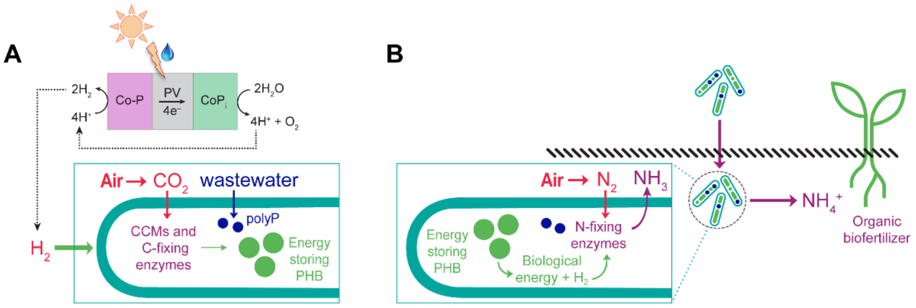

Fig. 4. The Bionic Leaf-**N**. (**A**) The Bionic-Leaf N combines H_2 from solar water splitting with CO_2 to produce polyhydroxybutyrate (PHB) and then (**B**) draws on the PHB as internal energy and hydrogen supply to power the nitrogen fixation cycle to produce ammonia and solid N biomass. Once PHB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

unencumbered as reflected by exceptionally high nitrogen conversion activity (turnover frequency of 1.9×10^4 s^{-1} per bacterial cell and turnover number of ~ 9×10^9 bacterial cell^{-1}). The ammonia produced directly or from biomass breakdown can diffuse across the *X.a.* membrane and be used as living biofertilizer. The Bionic Leaf-**N** is of significant consequence 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 [17]. As an example, in a large 400-acre farm trial for leafy vegetables, 130 lbs of N is needed per acre for crop growth. By replacing 90% of the chemical fertilizer (UAN = urea ammonium nitrate, 5.98 lb CO_2 produced per lb N for UAN) with the Bionic Leaf-**N**, 141 metric tons of carbon dioxide was prevented from being released into the atmosphere [1]. Additionally, the Bionic Leaf-**N** sequesters CO_2 from air in the form of PHB (–1.105 lb CO_2 / lb N) and thus the use of Bionic Leaf-N as a living biofertilizer is a carbon negative process. Beyond mitigating the carbon budget associated with crop growth the Bionic Leaf-**N** has an important future role in sustainable farming as the living biofertilizer avoids nitrogen runoff, and it is also able to fix P from wastewater [18] to allow for cyclic and renewable rotation of the biogenic elements of C, N and P.

Sustainable Manufacturing

Th HIB approaches reveals a path forward to creating a distributed and sustainable manufacturing industry. The powerful tool of synthetic biology allows the HIB approach to be generalized to 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—if you will, vitamins from thin air [19]. For solar manufacturing by the HIB approach, new science needs to be developed that meets the high throughput demands of scale for manufacturing processes. High mass fluxes of reactants and products are need for manufacturing and thus catalysts with high turnover rates and accelerated metabolic pathways of bioorganisms will be needed. The HIB approach need not be confined to the cell. In this case, outside of the cellular confines, enzymes will have to function with stability over long periods of time under manufacturing relevant conditions. Embodied in the catalysis and reactor designs are many challenges including the need to furnish products selectively, isolate those products, and capture CO_2 at low energy intensities. Ultimately, the science that underpins solar manufacturing must be cost effective over long-term operation.

Concluding Comments: The Sustainocene

The Holocene (‘recent whole’) period began 12,000 years ago with the introduction of human activity on our planet. From that time until circa 1800 CE, the presence of humans did not alter the natural systems of this world. Since 1800 CE, human activity has pushed this planet from the Holocene into what has been termed the Anthropocene period, an epoch when human interference with earth systems threatens the capacity of our biosphere to sustain life. The science and technology that created the Anthropocene now needs to be addressed with a science and technology that creates a new epoch—the 'Sustainocene'—a period of ecological sustainability, environmental integrity and the elimination of gross societal imbalances in poverty by providing a global population with access to energy, food and water. The connection of the Sustainocene with the need for new science for the poor is plainly evident from the Kaya Identity,

$$CO_2e = N \bullet (GDP/N) \bullet (E/GDP) \bullet (CO_2e/E)$$

where CO_2e = global CO_2 emissions, N = population, GDP/N = gross domestic product per capita, E/GDP = energy needed to maintain GDP and CO_2e/E = carbon footprint of the energy supply. For climate change to be stabilized, it is essential that CO_2e/E be minimized, i.e., that the new energy demand, E, for the underserved be sustainable owing to the addition of 6 billion to N in the Kaya Identity. The advances described herein establish that the Sustainocene is possible. However, more scientists need to embrace a science targeted to the poor where they will realize a plethora of new challenges and a fertile space for new discovery. In doing so, they will set out on the quickest path to stabilizing climate change and they will be the leaders of a historic change to a global chemical and energy infrastructure, one powered by the sun, air and water.

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