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Engineered and Artificial Photosynthesis: Human Ingenuity Enters the Game

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All oxygen-dependent life depends on photosynthesis. In addition to breathing the oxygen produced by photosynthesis, humans have been harnessing energy from photosynthesis for millennia. Since the beginning of human societal structures, human needs have driven the evolution of agricultural production, and they continue to do so. Recently, it has been suggested that agriculture can contribute substantially to human technological (nonnutritional) energy needs. This possibility raises concern because the projections of human energy needs argue convincingly that without large increases in energy conversion efficiency (ECE), land-grown biofuel production and food production will compete for land, a largely untenable compromise given the current nutritional status of the world's underdeveloped societies.

In addition to using the fuel provided by nature's photosynthetic process, humans have devised direct routes for harnessing solar energy including, for example, photovoltaic (PV) cells. These cells produce energy in the form of electromotive force (emf, electricity), which, although ideal for many applications, is not easily stored and used for fuel (e.g., in transportation). We posit that transformational progress toward meeting the goals of supplanting fossil fuels, providing energy security, and mitigating climate change can be made at the intersection of technology and biology. This intersection comprises artificial photosynthesis, other bio-inspired energy conversion processes, and the design of organisms that specialize in efficient biofuel production from solar energy. As outlined here, artificial constructs can contribute directly to solar energy conversion, can be incorporated into hybrid systems, and can inform the design of new photosynthetic organisms.

What Do We Mean by Efficient, and Why Isn't Natural Photosynthesis More Efficient?

The initial energy-conserving steps in the conversion of solar energy to either electricity or biomass can be described by elementary photophysical processes; the essential ones are shown in **Figure 1**. The absorption of light (red and green arrows) promotes an electron to a higher energy level, which leads to an excited state in which an electron is repositioned in spatial and energy coordinates and a positive charge (hole) is left behind. This is the transformation of solar to chemical energy; the electron is chemically reducing (low electrochemical potential), and the hole is chemically oxidizing (high electrochemical potential). In molecular systems, the further stabilization necessary to prevent wasteful relaxation back to the ground state involves moving the electron and hole farther apart; there is a concomitant loss of energy (illustrated by the dash-dotted arrows in **Figure 1**) necessary to drive this charge separation process. In typical PV cells, the hole and electron are separated and thereby stabilized by an internal electric field at the junction of the *n*- and *p*-type semiconductor materials. The energy associated with separating the charges (dash-dotted arrows in **Figure 1**) reduces the electrical energy available in the external circuit. Charge separation sets the stage for describing three efficiency-defining processes: a high fraction of the photons absorbed must yield charge separation (i.e., the quantum yield of charge separation must be high); the energy of the charge-separated state must be high; and recombination of the electron and hole, producing heat, must be much slower than chemical reactions making productive use of the oxidation and reduction potential (or slower than the conduction of charge in a PV device).

ECE is defined as the usable electrical or harvestable chemical energy output divided by the total solar energy incident on the organism or device. In terms of meeting human energy needs, which are usually expressed on an annual basis, it is convenient to calculate ECE using insolation (incident solar energy) per year summed over diurnal and seasonal cycles. ECE is a fundamental parameter that determines the area required to provide a specified amount of energy for human use. Some examples of the ECEs of

biofuel production by photosynthetic organisms and electrical work by a typical PV cell are listed in **Table I**.

Clearly, not all of the energy of incident sunlight can be converted into useful work. In addition to the efficiency-limiting processes mentioned above, other factors come into play. The ECE is limited first by the fraction of sunlight absorbed by the organism or device: photons having less energy than required for the lowest-energy absorption transition of the material will not be absorbed. This is illustrated by the pink arrow in **Figure 1**. The ECE is also limited because both photosynthetic organisms and simple PV devices such as silicon solar cells function as single-threshold systems. In other words, the energy of absorbed photons that is above the lowest excited singlet state of chlorophyll (or the conduction-band energy of a solar cell) is lost as heat during the electronic relaxation processes that populate the lowest excited state (see arrow labeled "Internal conversion" in **Figure 2** and the dashed arrow in **Figure 1**). In photosynthesis, this leads to a loss of about one-fourth of the absorbed energy. A threshold or bandgap of about 1.3 eV is optimal. The increase in chemical potential of the charge-separated state with increasing bandgap comes at the expense of the fraction of photons (in the pink arrow category in **Figure 1**) absorbed from the solar spectrum. The bandgap in water-oxidizing photosynthesis is about 1.8 eV, well on the high-energy side of optimal. Finally, as mentioned above, conversion devices—natural and artificial—sacrifice some of the potentially available energy in order to slow charge recombination reactions and drive desired chemical or electrical processes forward. As a result of these factors, illustrated by the dash-dotted arrows in **Figure 1**, a significant fraction of photon energy must be lost as heat in any conversion device. The best single-threshold photovoltaic devices have ECEs that approach the Shockley–Quiesser limit of about 30%, which was calculated taking all of the above considerations into account. In contrast, although the initial steps of plant and bacterial photosynthesis often have very high quantum yields, the ECE of natural photosynthesis is relatively low (maximally about 6% but usually observed to be <0.8%).

The apparent paradox of a high quantum yield and low ECE in natural photosynthetic systems can be resolved by analyzing the energy flow in the photosynthetic process presented in **Figure 2**, which qualitatively illustrates the energy losses from absorbed incident radiation during photosynthesis by a typical terrestrial plant leaf at full sunlight. Photosynthetic organisms have evolved by maximizing flexibility in metabolism and nutrient supply and are therefore able to adapt to diverse environmental conditions that are not necessarily consistent with overall energy storage efficiency. The physiological reactions required for steady-state maintenance of energized membranes and reproduction (that is, the biosynthesis of components that are not particularly energy-rich and the turnover of cellular components) are essential to the survival of the organism (**Figure 2**, arrow labeled "Growth and maintenance"). These processes require copious amounts of energy and resources, but do not directly produce harvestable, high-energy-content biomass for human use.

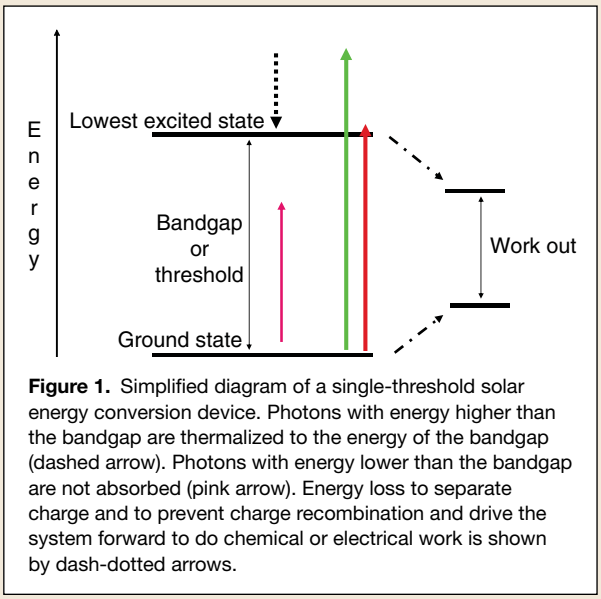

Figure 1. Simplified diagram of a single-threshold solar energy conversion device. Photons with energy higher than the bandgap are thermalized to the energy of the bandgap (dashed arrow). Photons with energy lower than the bandgap are not absorbed (pink arrow). Energy loss to separate charge and to prevent charge recombination and drive the system forward to do chemical or electrical work is shown by dash-dotted arrows.

Table I: Annual Biofuel Production and Energy Conversion Efficiency by Photosynthetic Organisms and Electrical Energy Production by a Photovoltaic Cell.

Oil Producer	Fuel Production [kg/(ha year)]	Energetic Equivalent [kWh/(ha year)]	ECE (%)
Oil palm	3,600–4,000	33,900–37,700	0.16–0.18
Jatropha	2,100–2,800	19,800–26,400	0.09–0.13
Tung oil tree (China)	1,800–2,700	17,000–25,500	0.08–0.12
Sugarcane	2,450	16,000	0.08
Castor oil plant	1,200–2,000	11,300–18,900	0.05–0.09
Cassava	1,020	6,600	0.03
Microalgae	91,000	956,000	4.6
Si-based PV cell		3×10^6	14.3

Source: References 14,15.
Note: ECE (energy conversion efficiency) is calculated by dividing the energetic equivalent by the energy content of the total solar spectrum averaged over 1 year incident on 1 hectare (ha) for a sunny climate at moderate latitude [21 million kWh/(ha year)] (Phoenix, AZ; http://rredc.nrel.gov/solar/old_data/nsrdb/redbook/). Si-based PV cells produce electricity, not fuel. We assume 80% of the hectare can be covered by solar collectors operating at 18% efficiency, 0% tilt. Comparing PV ECE with biological ECE requires knowledge of the efficiency of converting either fuel to electricity or electricity to fuel. Modern power plants can convert fuel to electricity at about 60% efficiency. Electrolysis of water to yield hydrogen and oxygen is the only commercial example of the conversion of electricity to fuel. Commercial electrolyzers can operate at 80% efficiency.

The evolution of natural photosynthesis was not driven by maximally efficient energy storage, but rather allowed organisms to tap into a new power source, solar energy, and thus to colonize and survive in new environments far from the geochemical energy sources that likely powered early life. In this view, natural photosynthesis can be thought of as an "add-on module" that probably appeared after many of the central metabolic and bioenergetic processes had been established. Although the fierce evolutionary struggle of photosynthetic organisms to prevail in their local surroundings has certainly tuned photo-

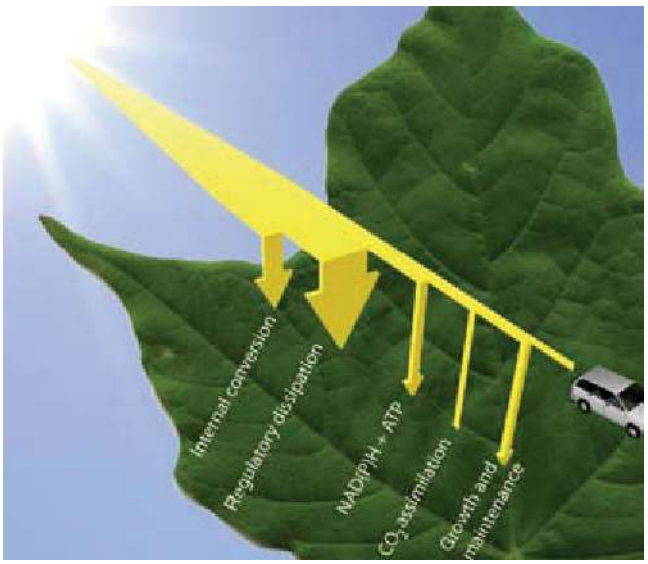

Figure 2. Simplified "energy flux" diagram for a typical terrestrial (crop) plant leaf under full sunlight, showing the losses to energy conversion efficiency (ECE) during major processes of photosynthesis. The losses are shown roughly in the temporal sequence in which they occur; the width of the arrows is qualitatively proportional to the percentage of energy lost. Internal conversion refers to the relaxation to the threshold indicated by the dashed arrow in Figure 1. Feedback from the three metabolic processes and the incident sunlight intensity strongly affects the magnitude of regulatory dissipation.

synthesis to work well with this "legacy biochemistry," there are apparent inefficiencies; evolution might not have explored fundamentally new pathways.

Several examples illustrate the energetic mismatch between the add-on module, photosynthesis, and legacy bioenergetics. The main chemical and electrochemical fuels of life [e.g., ATP and NAD(P)H] evolved under anaerobic conditions where an organism had to eke out a living on small redox gradients (like running a machine with a very low voltage battery). Photosynthesis made available both large redox gradients, spanning about 2.4 V in water-oxidizing photosynthesis, and highly energetic chemical species. This thermodynamic mismatch is apparent in Photosystem I, one of the major photosynthetic machines of cyanobacterial and higher-plant photosynthesis, where approximately 1.1 V (about 60% of the converted energy) is lost before the system comes into electrochemical steady state with the reduction of $NAD(P)^+$ to NAD(P)H. Even considering that electron transfer from water to NAD(P)H also stores some energy in ATP, the system operates at a very large "overpotential." The energy loss can be approximated by comparing the absorbed solar energy with the measured potentials of NAD(P)H and ATP and amounts to approximately 58% of the energy entering the photochemical reaction centers [see arrow labeled "NAD(P)H + ATP" in **Figure 2**].

Another example of apparent inefficiency is the water-oxidizing Photosystem II, the photosynthetic reaction center that makes the molecular oxygen that we breathe. This system is a marvel of thermodynamic efficiency in the sense that minimal overpotential appears to be necessary to oxidize water—a feat unmatched by any human-engineered catalysts—and only earth-abundant elements are used. However, even with elaborate control mechanisms, parts of the "machine" break down within 1 h under bright sunlight and must be removed from service for repair and then reassembled.

Energy stored in ATP and NAD(P)H is used mainly to take up and convert CO_2 into carbohydrates (also known as "fixing" CO_2) through a patchwork of ancient biochemical pathways known as the Calvin cycle (or C_3 cycle). The process itself can run on a relatively low driving force (low overpotential), but suffers from wasteful side reactions and low maximum rates. The key enzyme in this pathway, RuBisCO, not only catalyzes the reduction of CO_2 to high-energy compounds, but also reacts with O_2, acting as an oxygenase and leading to the "unfixing" of reduced carbon back to CO_2 and the concomitant loss of energy in the process. In addition, RuBisCo is a notoriously slow enzyme, with a low affinity to CO_2, and thus represents a major rate limitation for the entire photosynthetic process, especially under conditions where CO_2 is limited. The legacy biochemistry of the Calvin cycle is simply unable to cope with the large influx of solar energy available from photosynthesis. Rather than solving the problem of inefficient carbon fixation, C_3 plants have evolved control mechanisms to dissipate as heat much of the light energy they absorb under conditions where CO_2 availability limits photosynthesis. Such dissipation is necessary because, in addition to driving down the CO_2 concentration and thereby increasing the oxygenase activity, excess light can lead to undesired chemistry (e.g., formation of reactive oxygen species). Under full sunlight, this energy dissipation can lead to a 50–80% lowering of the quantum yield (and therefore of the ECE) of photosynthesis (arrow labeled "Regulatory dissipation" in **Figure 2**).

Some plants, algae, and cyanobacteria have partially responded to the unfortunate situation involving RuBisCO with a metabolically expensive patch, in which photosynthetic energy is used to concentrate CO_2 so that it can be processed more efficiently by RuBisCO; this alternative provides some improvement but is not found in all agriculturally important plants.

Finally, as mentioned earlier, there are losses due to the energy needed for growth and maintenance of the plant, resulting in a typical ECE for land plants of 0.3–0.8% (see **Table I**, which refers to biofuel production only, and Reference 4).

Interestingly, some algae and cyanobacteria (collectively known as microalgae) have remarkably higher ECEs than terrestrial plants (**Table I**). This is because some of the ECE-limiting factors discussed above are more important for large land plants than they are for microalgae in aqueous environments. For example, CO_2 fixation in leaves is often limited by CO_2 diffusion, whereas uptake of inorganic carbon is much less limiting in small organisms with much larger surface/volume ratios. Moreover, because the solubility in water of CO_2 is much higher than that of O_2, the carbon fixation/carbon oxidation ratio of RuBisCO is much more favorable in aqueous environments. In addition, smaller organisms require less energy investment for chemical transport and for generation of a "skeleton," and they tend, overall, to have better ECEs than terrestrial plants. As shown in **Table I**, a far better ECE can be achieved by culturing microalgae for biofuel production than by growing terrestrial plants for this purpose.

Indeed, understanding the factors that limit ECE could lead to genetic engineering efforts that enhance biofuel production in living systems. It can be seen from **Figure 2** that regulatory dissipation is the largest loss mechanism. The need for regulatory dissipation arises in large part from the limited kinetic competency of CO_2 assimilation. Engineering improved kinetics of CO_2 assimilation can thus reduce this loss and, further downstream, the loss of energy in plant

growth and maintenance. Much more needs to be understood about photosynthesis (and plant metabolism in general) to make larger gains, perhaps involving radical reengineering of plants to decrease the loss of energy in coupling the photochemical events to NAD(P)H and ATP synthesis.

How Can Artificial Photosynthesis Be Used To Address These Issues?

Efficient water oxidation is one of the holy grails of sustainable solar fuel production. As mentioned above, water oxidation in photosynthesis is essentially a single-threshold process and is therefore subject to the Shockley–Quiesser limit of about 30% ECE. This value is further reduced to about 10% by the use of the two photosystems (two quanta per electron), each with nonoptimal thresholds of about 1.8 eV. It has not been demonstrated that this tandem system is necessary to split water; it is almost certainly a legacy of the evolution of type 1 (Photosystem I, PS I) and type 2 (Photosystem II, PS II) reaction centers. To explore the two-quanta-per-electron issue, artificial reaction centers are being used in conjunction with dye-sensitized semiconductor photoelectrodes (Grätzel-type photoanodes) to determine the overpotentials necessary to drive water oxidation and H_2 production at rates comparable to the solar photon flux, using biological and bio-inspired catalysts. Once the electrochemical parameters that optimize single-photon-per-electron water oxidation are determined, efforts already underway to reengineer photosynthetic membranes will be better informed.

Reengineered photosynthesis could involve pathways that are not limited by legacy biochemistry. For example, only three enzymatic steps, all catalyzed by NAD-linked dehydrogenases, are required to oxidize methanol to CO_2. If remodeled to run backward and be driven directly by PS II, which could be engineered to have a slightly more reducing potential, this process would accomplish one-photon-per-electron water oxidation and fuel production. There would be a small penalty associated with moving the 1.8 eV chlorophyll excited state higher (and further from the optimal bandgap) to increase the reduction potential, but that would be more than offset by achieving one-photon-per-electron photochemistry.

Artificial photosynthetic constructs and bio-inspired catalysts can serve as links between human-engineered and biological processes and thereby open the door to new carbon-fixing pathways. In the example above, the remodeled NAD-linked enzymes driven by sustainably produced emf (electricity) could direct the reduction of CO_2 to methanol. If methane mono-oxygenase were added and the reaction driven backward, the product would be the world's most energy-rich carbon-based compound (on a per-carbon basis): methane. The advantages of enzymes (or, someday, bio-inspired catalysts) that oxidize water and direct the synthesis of energy-rich fuel at room temperature—and that require only electrical driving force and redox equivalents—set up an overarching challenge in this field: coupling the appropriate redox enzymes to sources of emf. Toward this end, artificial photosynthetic reaction centers have been demonstrated to photo-inject electrons or holes into semiconductors. These processes convert molecular redox potentials of the kind used by redox enzymes to emf in metallic conductors. This field is advancing rapidly. Hoped-for breakthroughs include the design and synthesis of new high-potential electron mediators inspired by the tyrosine/histidine system found in water-oxidizing photosynthesis and the design, synthesis, and assembly of artificial active sites of enzymes directly on electrodes. The development of ultrahigh-surface-area materials that could provide the three-dimensional structure necessary to recognize transition states, and thereby guide reactants to desired products, and also conduct emf to drive the reactions would make available efficient electricity-to-fuel technology. Corrosion-resistant semiconductors having valence-band "holes" at the potential necessary to oxidize water and conduction bands that are electrochemically negative enough to reduce protons to hydrogen (hydrogen production is a "thermodynamic" proxy for the synthesis of all energy-rich, carbon-based fuels) present a significant challenge to materials science but would enable solar water splitting.

Such work illustrates the interplay between natural and artificial constructs that could lead to new materials or compounds. For example, the ECE of the Grätzel PV cell would be substantially improved by a high-potential electron relay mimicking the tyrosine/histidine-based system used by nature in PS II.

Energy Conversion by Hybrids of Natural and Artificial Systems

Once effective "molecular wires" or other electron relays between metallic conductors and genetically engineered biological catalysts can be made, microorganisms dedicated to synthesis could provide a renewable source of catalytic material. In this way, the self-assembly, self-repair, and self-replication characteristics of living things would be harnessed to meet human needs.

Recent discoveries indicate that nature might, in fact, have already outlined a strategy for the exchange of energy in the form of emf between human-engineered sources and biochemical processes. Geobacteria appear to produce pili that make electrical connections across their plasma membrane, connecting the redox chemistry inside the organism to an external electron sink. Imagine that, when coupled to an electrode with appropriate wiring to complete the circuit, an applied potential could drive metabolic processes inside the organism. Such a system in which the organism was genetically reengineered to produce biofuel would be self-perpetuating in the biological sense but inexorably linked to human-engineered energy sources that are efficient and robust—a true hybrid.

In addition to providing catalytic paradigms for much of the mainstream energy-processing chemistry that humans use, nature almost certainly has found catalytic pathways for other chemical processes that are key to the efficient and sustainable use of Earth's resources. Nitrogen fixation is one obvious example. Another is digestion of cellulose to simple sugars. Powerful new tools such as metagenomics are being used to discover new organisms that have metabolic pathways tuned to match their local niches. Indeed, we have undoubtedly only just begun to learn from nature.

For further information on engineered and artificial photosynthesis, the interested reader can consult References 1–13.

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