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Comparing Photosynthetic and Photovoltaic Efficiencies and Recognizing the Potential for Improvement

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Comparing photosynthetic and photovoltaic efficiencies is not a simple issue. Although both processes harvest the energy in sunlight, they operate in distinctly different ways and produce different types of products: biomass or chemical fuels in the case of natural photosynthesis and nonstored electrical current in the case of photovoltaics. In order to find common ground for evaluating energy-conversion efficiency, we compare natural photosynthesis with present technologies for photovoltaic-driven electrolysis of water to produce hydrogen. Photovoltaic-driven electrolysis is the more efficient process when measured on an annual basis, yet short-term yields for photosynthetic conversion under optimal conditions come within a factor of 2 or 3 of the photovoltaic benchmark. We consider opportunities in which the frontiers of synthetic biology might be used to enhance natural photosynthesis for improved solar energy conversion efficiency.

Sunlight is the most abundant and sustainable source of energy available to humanity. Earth receives solar energy at the rate of approximately 120,000 TW (1 TW = 10^{12} W) in a highly reliable and distributed fashion. This vastly exceeds the current annual worldwide energy consumption rate of ~15 TW and any conceivable future needs in this century (*1*–*3*). However, sunlight is dilute; the yearly averaged solar power striking the Earth's surface is about 170 W per square meter, which varies depending on geographical location (*4*). Devising methods by which to efficiently capture and store this energy for societal use is one of the great challenges of our age. There is general agreement that no one approach is capable of solving our energy needs for the future and that a mix of sustainable technologies will be required (*5*).

There is considerable confusion, especially in the popular press, about how to compare the efficiency of solar energy capture in photovoltaic devices with a corresponding characteristic of photosynthetic organisms. The problem hinges on the different assumptions and conditions underlying the definition of efficiency in each case (*6*, *7*). To facilitate direct comparisons between photosynthetic and photovoltaic (PV) systems, we provide consistent definitions and examine the major factors that define the efficiencies of both processes—first considering current technology, then looking forward to possible strategies for improvements. In all cases, we consider the efficiency of harvesting the entire solar spectrum as a basis for comparison.

We focus exclusively here on conversion efficiency. However, the total integrated cost of the systems, including land, water, capital, operations and maintenance, waste disposal, transmission, transportation and storage, as well as risks from manufacturing and possible interactions with the food supply and climate change, must also be considered. Therefore, the technology with the highest efficiency may not necessarily be the best choice to implement in a given situation. Ultimately, a comparison of solar energy options must come from the perspective of a complete life-cycle assessment in order to evaluate the full suite of energy inputs, infrastructure and renewal requirements, and environmental factors, including greenhouse gas balance. This is a critical and active area of research for both photosynthetic and PV systems (*8*, *9*), but currently there is little consistency in the methods used. Differences in assumptions about efficiency terms, life-cycle inventory components, and systems boundaries create large variations in the metadata generated from the many concomitant efforts.

Comparing Photosynthetic and Photovoltaic Efficiencies

Efficiency is a concept that is deceptively simple yet can be elusive for comparisons between such different systems as living organisms and photovoltaic cells. The solar conversion efficiency of a PV device can be directly measured with high accuracy and is usually quoted by researchers and manufacturers in terms of power: electrical power out (W/cm^2) divided by incident solar irradiance (W/cm^2) measured over the entire solar spectrum. This instantaneous metric, measured at peak solar intensity, does not include energy storage and transmission. In contrast, natural photosynthesis stores energy in the chemical bonds of its molecular products and uses much of this energy to sustain and replicate the organism, typically over a defined growing season.

A more direct comparison of PV and photosynthetic solar energy conversion efficiencies would consider a process in which PV also stores energy in chemical bonds. Application of PV-derived energy to electrolysis of water is a good choice for this purpose: Existing commercial electrolyzers afford accurate efficiency benchmarks, and the free energy needed in order to split H_2O into H_2 and O_2 (ΔG° = 1.23 eV) is essentially equal to the free energy change associated with photosynthesis [ΔG° = 1.24 eV for $CO_2 + H_2O$ to $(CH_2O) + O_2$, where (CH_2O) is shorthand for carbohydrate].

The power conversion efficiency of present commercial single-junction (single photosystem) silicon solar cell modules is typically 18 ± 2% (*10*). This value pertains to peak solar intensity (1 kW/m^2), with an AM1.5 spectral distribution or solar zenith angle of 48.2° (sunlight passing through 1.5 atmospheres). The efficiency of a PV module changes during the day and throughout the year because of the changing solar zenith angle, and the PV efficiency averaged over a 1-year cycle is about 95% of the maximum AM1.5 value. Modern commercial electrolyzers have efficiencies as high as 80% [based

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on heat of combustion of H_2 to H_2O in liquid form at atmospheric pressure and 25°C, standard temperature and pressure (STP) conditions]. Thus, an annual averaged efficiency for solar water splitting by PV-driven electrolysis would be about (0.18) × (0.95) × (0.8) ~ 14% (*11*). This assumes that there is no mismatch between the photovoltage generated by the PV array and the voltage required for electrolysis. Present Si PV modules arranged in electrical series would suffer mismatch losses as high as 20 to 30%, bringing the overall H_2O splitting efficiency down to ~10 to 11%. This constitutes the first benchmark to compare with the efficiency of photosynthetic fuel production. As discussed below, ongoing research is providing opportunities to construct PV devices with considerably higher efficiencies.

Several different measures of efficiency have been used in describing natural photosynthesis. The quantum efficiency is the percentage of absorbed photons that give rise to stable photoproducts. Photosynthetic organisms typically can operate at nearly 100% quantum efficiency under optimum conditions (*12*). For comparison with PV electrolysis over an annual cycle, the energy efficiency of photosynthesis is a more useful parameter and is defined as the energy content (heat of combustion of glucose to CO_2 and liquid H_2O at STP) of the biomass that can be harvested annually divided by the annual solar irradiance over the same area. Using this definition, solar energy conversion efficiencies for crop plants in both temperate and tropical zones typically do not exceed 1% (*7*, *13*), a value that falls far below the benchmark for PV-driven electrolysis. Higher 3% annual yields are reported for microalgae grown in bioreactors (*14*).

Short-term (rapid growth phase) efficiencies measured during the growing season are higher, reaching 3.5% for C3 and 4.3% for C4 plants (*7*), and perhaps 5 to 7% for microalgae in bubbled bioreactors (*15*). These efficiencies are measured in the absence of restrictions imposed by plant life-cycle regulation or by light and gas exchange limitations in the case of algae. Even so, these values fall below theoretical limits and ultimately limit the net annual productivity. Most natural photosynthetic systems store solar energy only during a growing season; efficiencies measured during that period must therefore be reduced accordingly to make valid comparisons on an annual basis, although the extent of reduction depends on the type of crop and the environmental conditions.

Theoretical Limits to Solar Energy Conversion

Both PV and natural photosynthetic systems obey the same fundamental laws of thermodynamics, which impose firm upper bounds on efficiency. There is an extensive literature on each process dating back over 50 years, and although the formulations differ substantially, the overall conclusions are similar. Following pioneering studies by Duysens (*16*), many authors have examined the thermodynamics of photosynthesis, most recently Knox and Parson (*17*). Shockley and Queisser pioneered studies on the maximal efficiency of PV cells (*18*); a recent analysis by Hanna and Nozik considers multiple-junction cells and other modern developments (*19*).

The first step in each system's energy conversion process is light absorption, which is governed by quantum mechanics. Figure 1 shows a reference solar spectrum at the surface of the Earth, with transmission spectra of a cyanobacterium and a silicon cell superimposed. The radiant energy intercepted by the chlorophyll, carotenoids, and other accessory pigments in oxygenic photosynthetic organisms is usually limited to the visible region of the spectrum (400 to 700 nm). Photosynthetic organisms thus access only ~50% of the incident solar energy (*7*, *20*, *21*). The silicon cell has a broader absorption range, extending from the ultraviolet (UV) to nearly 1200 nm in the near-infrared (near-IR).

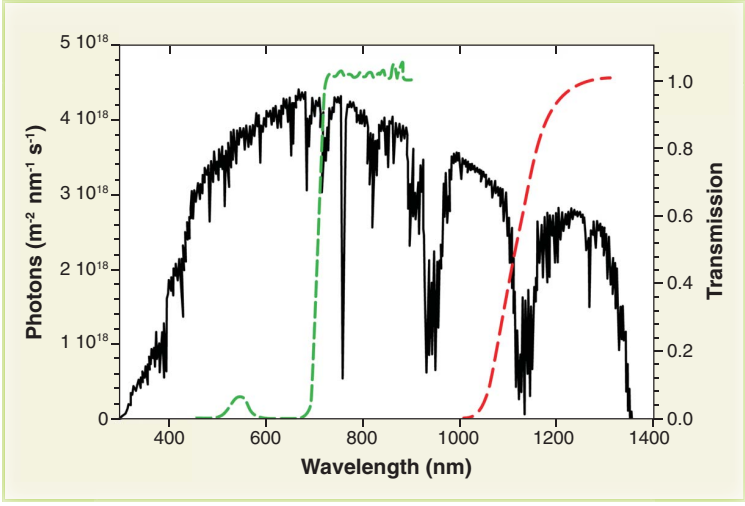

Fig. 1. The photon flux spectrum of solar radiation reaching Earth's surface (plotted in black) (*66*) and the transmission spectra of a natural photosynthetic organism, the cyanobacterium *Synechocystis* PCC 6803 (green dot-dashed line) and of crystalline silicon [red dashed line, redrawn with permission from (*67*)]. The transmission spectra show that both the cyanobacteria and silicon absorb almost all photons at shorter wavelengths above the threshold energy but transmit photons at longer wavelengths below the threshold energy. The cyanobacterial sample has a window of transmission in the green region of the spectrum that causes the culture to appear green. The cyanobacterial sample had an absorbance of 3.4 at 678 nm and was digitally corrected for scattering.

Thermodynamics furthermore dictates that not all the energy in each absorbed photon can be captured for productive use. Figure 2 shows the relevant energy diagrams. In photosynthetic organisms, absorption initially creates an excited state of chlorophyll or an accessory pigment. Although photons with blue wavelengths may be efficiently absorbed, ultrafast internal conversion processes relax higher excited states through release of heat to the energy of the lowest (reddest) absorption band. Similarly, conventional semiconductor-based PV cells can absorb photons with energy equal to or greater than the bandgap separating the valence-band from the conduction-band, but any photon energy in excess of the bandgap is lost as heat. Thus, both systems have a threshold energy that defines attainable light absorption, conversion efficiency, and energy storage capabilities.

When these considerations are included in a more detailed thermodynamic analysis using the entire solar spectrum, a single-junction PV system has a maximal instantaneous power conversion efficiency of ~32% at one-sun intensity and an AM1.5 spectral distribution, the so-called Shockley-Queisser limit (*18*). The Shockley-Queisser treatment is the isothermal equivalent of the Carnot cycle and assumes that all processes are reversible (no overpotentials, no dissipative losses), with the consequence that extracting chemical or electrical work from the system would be infinitely slow. In a realistic photoelectrolysis cell based on a single-threshold semiconductor photoelectrode (in direct contact with water) that generates hydrogen and oxygen at finite rates, the overvoltage would be finite. At unconcentrated solar intensities, the current density is relatively low (<35 mA cm^{-2}), so that an overvoltage of ~0.15 V is a reasonable assumption; this would decrease the maximum Shockley-Queisser efficiency for a photoelectrolysis cell to ~24% (*19*).

A theoretical limit of ~ 12% for the efficiency of photosynthetic glucose production from CO_2 and water (based on free energy) can be calculated by considering the chlorophyll band-edge absorption and the two-photosystem structure of oxygenic photosynthesis (*6*, *13*). Taking into account the known losses in light harvesting, overpotentials, and respiration, the maximum limit to photosynthetic efficiency is reduced to 4.6 and 6.0% for C3 and C4 plants, respectively (*7*). Short-term (rapid-growth phase) conversion

efficiencies come within 70 to 75% of meeting these limits. The passive diffusion of CO_2 at atmospheric concentration will set a conversion limit for fixation in both photosynthesis and artificial devices. Indeed, dense stands of rapidly photosynthesizing crops such as corn or soybean can lower CO_2 levels within the canopy 50 parts per million (ppm) or more below ambient (*22*), suggesting that CO_2 delivery affects the rate of carbon fixation. Given these constraints, opportunities to enhance photosynthetic productivity lie in the development of plant and microalgal systems that achieve sustained CO_2 fixation at yields close to the theoretical limits. Further productivity gains in both photosynthetic and PV systems could potentially be realized by designing systems that reset the limits to energy conversion as described below.

Improved System Design Raising Theoretical Limits

A key opportunity for raising the efficiency ceiling in PV systems lies in replacing single-junction devices with tandem cells optimized for water oxidation and hydrogen production. This approach could give efficiencies approaching 40% (free energy basis) as overvoltages approach zero (*19*, *23*). Further increases in PV efficiencies might be obtained by devices that use the blue and near-UV region of the solar spectrum more effectively or capture the energy of the sub-bandgap IR photons. Prospects under study include hot-carrier solar cells, intermediate-band solar cells, multijunction tandem architectures, and absorbing media that generate multiple charge carriers per absorbed photon. In these cases, the theoretical thermodynamic limit set by the second law reaches 66% at one-sun intensity (*24*, *25*), with corresponding increases in the yield of electrochemical products.

Turning to photosynthesis, one straightforward strategy for improving the efficiency limit would involve tuning the light-absorbing pigments to extend the range of solar light absorption (*26*). A related, substantial source of inefficiency arises from nature's use of two photochemical systems connected in series to generate the electric potential difference required to split water and reduce nicotinamide adenine dinucleotide phosphate ($NADP^+$). The effective bandgaps (absorption thresholds) of the two photosystems are similar. In practical terms, this means that the two photosystems compete for the same regions of the solar spectrum, cutting the energy efficiency nearly in half compared with what might be achieved if the bandgaps were different and optimized to use different regions of the spectrum (*19*, *27*).

Photosynthesis is unique in its capacity to produce a diverse array of complex organic compounds (leading to replication of the organism) through light-driven CO_2 reduction. There is no PV device that can deliver comparably selective carbon-fixation photochemistry, nor of course can PV devices replicate themselves. Although it can be argued that self-replication represents a real advantage for natural photosynthesis, it is also clear that the structure and function of the photosynthetic apparatus are limited by the need to operate within a living organism, for which they were tailored by evolution. The comparatively low efficiency of natural photosynthesis may result partly from the "legacy biochemistry" photosynthetic organisms inherited from earlier non-photosynthetic organisms that used biochemical pathways with redox cofactors not optimally matched for photochemical processes (*28*). Some factors that limit the efficiency of natural photosynthetic systems are intrinsic to the basic structure and organization of the photosynthetic apparatus and would require a major re-engineering to improve, whereas other improvements may be attained by more straightforward adjustments in the structure of the organisms or the growth conditions. Although this approach may seem daunting, agricultural breeding has been steadily achieving these goals for millennia, albeit primarily for food production, and typically not necessarily for high-efficiency energy storage. Because we have only just started breeding or engineering plants and algae for fuels production, it is likely that substantial improvements are feasible.

Photosynthetic organisms in the wild are selected through evolution for reproductive success, not for high biomass production in plant monocultures in which competition for resources (including light) is, in many cases, a disadvantage (*29*). Likewise, crop plants have been bred for various properties of the harvestable product but not for overall photosynthetic efficiency, while being nurtured by intensive agricultural practices that use substantial inputs of fossil fuels. Consequently, photosynthetic rates are often limited or down-regulated even below the theoretical limits imposed by the slowest reactions of CO_2 fixation and electron transport, leading to strategic down-regulation of productivity. This problem could be alleviated with breeding or engineering, even without radical changes to the photosynthetic apparatus (*7*, *30*). An interesting example of the importance of regulatory strategy is the acclimation of plants to higher CO_2 levels. In principle, the recent increase in atmospheric CO_2 levels should alleviate limitations of photosynthesis at the enzyme ribulose-bisphosphate carboxylase-oxygenase (RuBisCO); however, these gains may not be realized in plants that evolved to use the lower CO_2 levels that prevailed before the industrial revolution (*31*). This lack of acclimation to current and future CO_2 levels, which results in kinetic mismatches among the component processes of photosynthesis, is an obvious target for plant breeding and engineering. Further, cellular growth and maintenance of the organism can also be viewed as a loss of at least 30% of the stored energy (*7*). Part of this energy is used to synthesize large quantities of RuBisCO to compensate for the enzyme's relatively low catalytic rate constant.

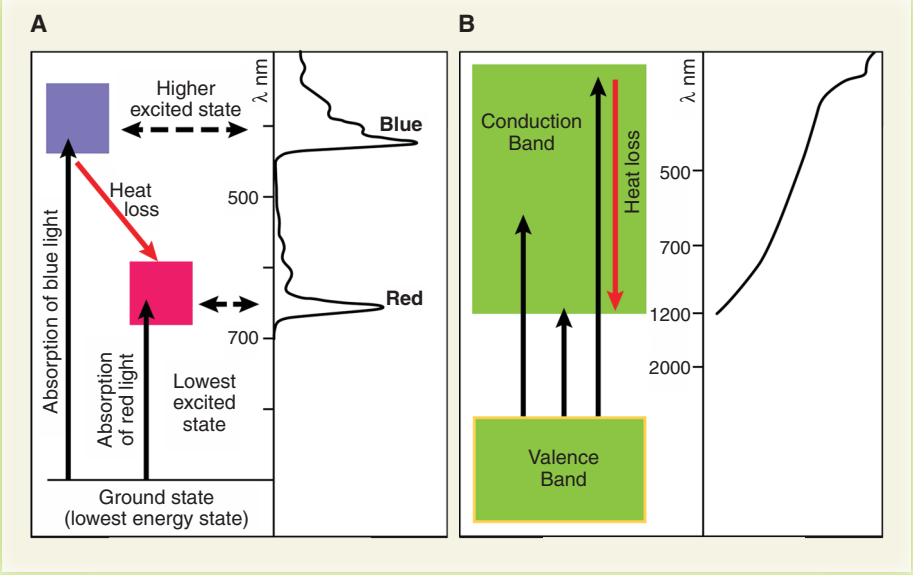

Fig. 2. Comparison of the threshold properties of photosynthetic and silicon-based PV systems. (**A**) Energy-level diagram for chlorophyll *a*, the major pigment found in most oxygenic photosynthetic organisms. The excited state is populated by blue light absorption and rapidly relaxes through heat loss to the energy level accessed by red light absorption, which is the effective threshold for energy storage. An absorption spectrum for chlorophyll *a* is shown for comparison. (**B**) Energy-level diagram for crystalline silicon, which is characteristic of the band structure of a semiconductor. The threshold absorption energy just bridges the bandgap (middle black arrow). Photons with a range of higher energies can still be absorbed, but their energy in excess of the bandgap is lost as heat before it can be stored. An absorption spectrum of silicon is shown for comparison (*67*).

Another instance of inefficiency in natural photosynthesis occurs when RuBisCO fixes the competitive substrate O_2 instead of CO_2, initiating the energy-intensive recovery process of photorespiration (*32*). Photorespiration can consume up to 25% of the initially stored energy (*7*). Some cyanobacteria, algae, and plants have evolved CO_2-concentration processes that largely circumvent photorespiration (*33*, *34*). However, these processes also entail an energetic cost that prevents realization of the entire advantage. In C4 photosynthesis, CO_2 is initially fixed into compounds with four carbon atoms (hence, the term "C4") and subsequently released at high concentrations near RuBisCO, where it competes more effectively with O_2 and reduces the oxygenation reaction substantially (*35*, *36*). Efforts are currently underway to introduce C4 photosynthesis or other carbon-concentrating systems into higher plants where they are currently lacking (*35*). If successful, these efforts may not only increase maximal photosynthetic rates and efficiencies directly but could reduce the large investment of energy and nutrients that C3 plants make in the synthesis of RuBisCO.

The amount of photorespiration can also potentially be reduced by engineering improved versions of RuBisCO with higher specificity for CO_2 over O_2, although this has proven difficult (*36*). A promising approach is the insertion of the *Escherichia coli* pathway for glycolate catabolism into *Arabidopsis* chloroplasts, introducing a bypass of the normal photorespiratory pathway by converting glycolate to glycerate directly in the chloroplast (*7*, *37*). Additionally, natural variants of RuBisCO that are better suited to current and anticipated CO_2 levels may be useful (*38*). Photorespiration also might be virtually eliminated by using flue gases from fossil fuel– or biomass-burning installations (such as power plants) as input gases for microalgal-based photobioreactor systems (*39*). These flue gases typically comprise ~10% CO_2, a concentration sufficient to suppress photorespiration almost completely.

All natural photosynthetic organisms contain light-gathering antenna systems, in which specialized pigments (typically several hundred) collect energy and transfer it to a reaction center where photochemistry takes place (*6*, *40*). With so many pigments absorbing light, full sunlight rapidly exceeds the capacity of the photosynthetic apparatus to process the influx of energy. In leaves in full sun, up to 80% of the absorbed energy must be dissipated or risk causing serious damage to the system (*41*). Plants have evolved a variety of mechanisms for dealing with this excess energy, including non-photochemical quenching pathways to prevent damage (*42*) and repair mechanisms if damage to reaction center proteins has occurred (*43*). However, the consequence is that surface cells exposed to the most light dissipate much of the available energy, whereas cells in lower layers remain starved for light. This overly aggressive capture of light may have an evolutionary advantage (for example, by shading competitors), but it decreases the overall efficiency of energy storage.

To address this issue, research efforts are underway in microorganisms to reduce the size of the antenna system (*44*, *45*). Truncated light-harvesting antennas can simultaneously reduce the problem of saturation at the surface and reduce shading deep in the water column, permitting more uniform illumination of the culture. In crop plants, modifying plant architecture can allow more light to pass to lower levels of the canopy, although lowering the chlorophyll content may be a more robust way to promote light energy distribution and canopy photosynthetic efficiency (*46*).

As noted earlier, plants and algae are generally restricted to absorbing visible light. Some species of cyanobacteria possess variants of chlorophyll that absorb further into the near-IR (740- to 750-nm wavelength range), increasing the amount of solar energy that can potentially be stored (*26*, *47*, *48*). Reducing the size of the antenna as discussed above might make it possible to expand the absorption spectrum without increasing saturation effects.

Synthetic Biology

The techniques of synthetic biology (*49*) may allow a more radical redesign of the photosynthetic apparatus for both bioenergy and food production applications. As mentioned above, the two photosystems required for oxygenic photosynthesis compete for the same wavelengths of light, reducing overall photochemical efficiency. An ambitious modification would be to maintain the two photosystems but engineer one of them to use the bacteriochlorophylls found in many anoxygenic photosynthetic organisms, which have absorption maxima that extend out to ~1100 nm. Figure 3 presents a schematic il-

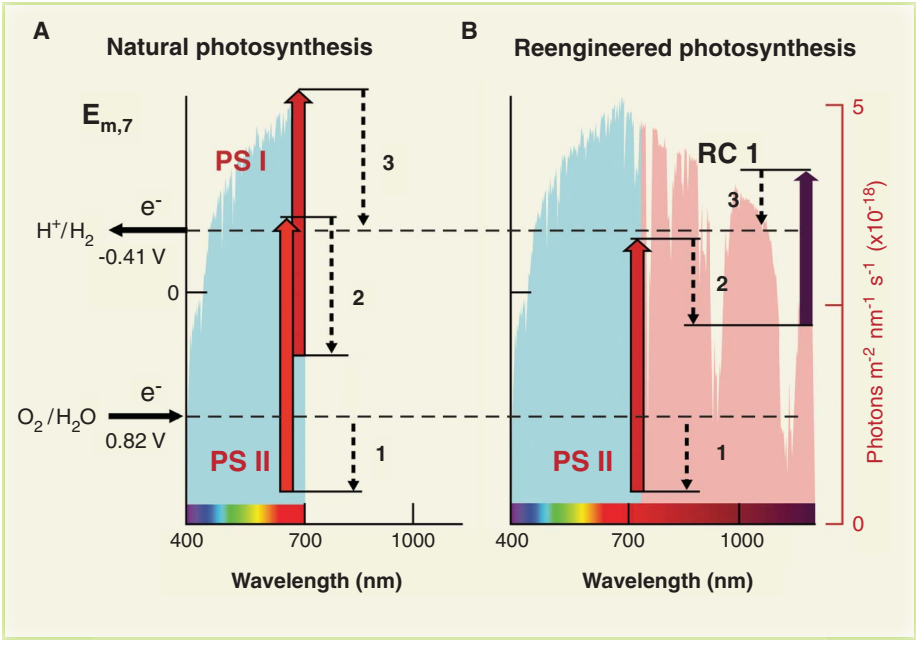

Fig. 3. (**A**) Photoelectrochemical energy capture diagram for photosynthesis and (**B**) photosynthesis reengineered following the thermodynamic principles in (*19*) for improved efficiency. The lengths of the upward arrows mark the initial photoinduced ground-to-excited-state electrochemical energy change of the reaction center primary donor chlorophylls. The position of the arrows along the wavelength axis is fixed by their length and is approximately at the red-most absorption edge of these chlorophylls. In (A), the vertical positions of the bases of the upward arrows reflect the approximate reduction potentials for the radical cation of the primary donor chlorophylls of photosystem I and photosystem II. In (B), the vertical and horizontal positions of the upward arrows are optimized for photosystems operating in tandem and providing 800 mV of overpotential to drive a chemical reaction having ΔG^0 of 1.23 eV that converts solar energy to electrochemical potential. The lengths of the downward dashed arrows indicate intrinsic free-energy losses associated with charge separation and electron transfer between photosystem II and reaction center I (arrow 2) and the overpotential necessary to drive the chemical oxidation-reduction reactions (arrows 1 and 3). In (A), electron transfer between the photosystems (dashed arrow 2) is associated with an energy-conserving ATP-coupling site. The background shows the portion of incident solar photons captured in each case. In (B) reengineered photosynthesis, photosystem I is replaced by a new reaction center, RC1, with farther-red-absorbing pigments. This increases the efficiency of photosynthesis by approximately doubling the solar photon capture and, using this biological version of a tandem cell, better matching the solar spectrum to the electrochemical work. For this illustration, reaction centers using chlorophyll *d* and bacteriochlorophyll *b* would be optimal for driving the redox catalysts.

lustration of a radically redesigned system in which the two photosystems have complementary optical spectra, conferring pseudotandem photocell function. The extent to which true tandem-cell efficiency were achieved would depend on the success of directing energy transfer from antennas absorbing 400- to 730-nm and 730- to ~1100-nm photons to different reaction centers. Wiring each antenna to the appropriate reaction center could potentially take advantage of structures in which exciton coupling or quantum coherence effects direct energy flow more efficiently (*50*). An optimum configuration could mimic a two-junction tandem photovoltaic cell (*19*).

Substantial improvements can be envisaged even within the context of the two-photosystem architecture of current oxygenic photosynthesis. As discussed earlier, for example, the carbon fixation process is currently limited by photorespiration associated with the low substrate selectivity of RuBisCO. Although RuBisCO is found in all oxygenic photosynthetic organisms, it might nonetheless be possible to introduce a different carbon-fixation cycle in place of the Calvin-Benson cycle (*51*, *52*). Most of the known alternative cycles are highly O_2 sensitive and are probably unsuitable for organisms that live in the presence of oxygen. However, the hydroxypropionate cycle found in filamentous anoxygenic phototrophs is not O_2-sensitive (*53*). An alternative is to forego production of reduced carbon storage products and produce H_2 by reduction of H^+. This process can be accomplished by using hydrogenase enzymes (*54*) or platinum nanoparticles (*55*) that are tethered to photosystem I. Because most hydrogenase enzymes are destroyed by O_2, re-engineering this system to be less O_2-sensitive is an important objective (*56*, *57*). In addition, a range of promising, O_2-tolerant transition metal catalysts are being developed (*58*). An intermediate enzymatic approach that is under investigation would treat CO_2 as an electron acceptor but reduce it only to the level of formate by using the enzyme formate dehydrogenase (*59*). The production of either hydrogen or formate may at the same time reduce the problem of light saturation because these systems have intrinsically very high capacity and could be capable of processing the electrons delivered by the reaction centers at a much higher rate than that of the RuBisCO-based C3 carbon-fixation cycle.

Outlook

We have sought here to make the most consistent comparison possible between the fundamental solar energy storage efficiencies of photovoltaic and photosynthetic systems. In this context, the efficiency advantage clearly goes to photovoltaic systems. However, there is clearly need to apply both in the service of sustainable energy conversion for the future. Approaches in which photovoltaics are coupled to redox chemistry in photoelectrochemical cells and even living organisms (*60*, *61*) also hold promise for solar fuels production. Numerous points of inefficiency in the natural system are amenable to improvement by using genetic engineering and more aggressive techniques of synthetic biology.

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