Solar Fuels via Artificial Photosynthesis

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CONSPECTUS

Because sunlight is diffuse and intermittent, substantial use of solar energy to meet humanity's needs will probably require energy storage in dense, transportable media via chemical bonds. Practical, cost effective technologies for conversion of sunlight directly into useful fuels do not currently exist, and will require new basic science. Photosynthesis provides a blueprint for solar energy storage in fuels. Indeed, all of the fossil-fuel-based energy consumed today derives from sunlight harvested by photosynthetic organisms.

Artificial photosynthesis research applies the fundamental scientific principles of the natural process to the design of solar energy conversion systems. These constructs use different materials, and researchers tune them to produce energy efficiently and in forms useful to humans. Fuel production via natural or artificial photosynthesis requires three main components. First, antenna/reaction center complexes absorb sunlight and convert the excitation energy to electrochemical energy (redox equivalents). Then, a water oxidation complex uses this redox potential to catalyze conversion of water to hydrogen ions, electrons stored as reducing equivalents, and oxygen. A second catalytic system uses the reducing equivalents to make fuels such as carbohydrates, lipids, or hydrogen gas. In this Account, we review a few general approaches to artificial photosynthetic fuel production that may be useful for eventually overcoming the energy problem.

A variety of research groups have prepared artificial reaction center molecules. These systems contain a chromophore, such as a porphyrin, covalently linked to one or more electron acceptors, such as fullerenes or quinones, and secondary electron donors. Following the excitation of the chromophore, photoinduced electron transfer generates a primary charge-separated state. Electron transfer chains spatially separate the redox equivalents and reduce electronic coupling, slowing recombination of the charge-separated state to the point that catalysts can use the stored energy for fuel production. Antenna systems, employing a variety of chromophores that absorb light throughout the visible spectrum, have been coupled to artificial reaction centers and have incorporated control and photoprotective processes borrowed from photosynthesis.

Thus far, researchers have not discovered practical solar-driven catalysts for water oxidation and fuel production that are robust and use earth-abundant elements, but they have developed artificial systems that use sunlight to produce fuel in the laboratory. For example, artificial reaction centers, where electrons are injected from a dye molecule into the conduction band of nanoparticulate titanium dioxide on a transparent electrode, coupled to catalysts, such as platinum or hydrogenase enzymes, can produce hydrogen gas. Oxidizing equivalents from such reaction centers can be coupled to iridium oxide nanoparticles, which can oxidize water. This system uses sunlight to split water to oxygen and hydrogen fuel, but efficiencies are low and an external electrical potential is required.

Although attempts at artificial photosynthesis fall short of the efficiencies necessary for practical application, they illustrate that solar fuel production inspired by natural photosynthesis is achievable in the laboratory. More research will be needed to identify the most promising artificial photosynthetic systems and realize their potential.
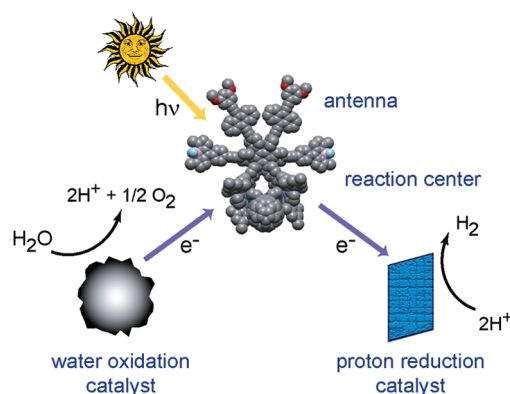
Introduction

A major challenge facing humanity is developing a renewable source of energy to replace our reliance on fossil fuels. Ideally, this source will be abundant, inexpensive, environmentally clean, and widely distributed geographically. Of the few potential energy sources that might meet these criteria, sunlight is the most attractive. The sun

delivers energy to the earth's surface at an average rate of ~120 000 TW, which is about 4 orders of magnitude larger than the current rate of worldwide technological energy use by humans. Although practical methods for conversion of sunlight to electricity exist, solar-generated electricity currently does not compete successfully with that from fossil fuels. In addition, the diurnal nature of solar radiation, the fluctuation of sunlight intensity at the earth's surface as a function of the season and weather conditions, and the diffuse nature of solar energy which makes it impractical for powering land vehicles require mechanisms for solar energy storage. This in turn will necessitate either great advances in batteries or other devices for storing electricity, or generation of fuels from sunlight. For example, hydrogen has been widely discussed as a fuel, and hydrocarbons have the advantages of very dense energy storage and well-established technologies for storage, distribution, and use. Unfortunately, there are currently no methods for solar fuel production that can compete with fossil fuel usage. Discovery of a fundamental scientific basis for new solar fuel technologies is vital.

There are many avenues for investigation of solar fuel production. One is artificial photosynthesis, the use of the fundamental science underlying photosynthetic energy conversion to design synthetic systems for converting light into stored chemical energy. Photosynthesis is the largest-scale, best-tested method for solar energy harvesting on the planet, and it is responsible not only for the energy stored in coal, petroleum, and natural gas but also for the energy that powers most of the biological world, and for the earth's oxygenated atmosphere. The overall efficiency of photosynthetic conversion of sunlight to stored energy in forms useful for human technology is rather low (a few percent at best): photosynthetic organisms evolved to grow and reproduce through overcoming environmental challenges and exploiting environmental opportunities, and not to make fuel for humans. However, at low light levels, the initial steps are quite efficient, and it makes good sense to look to the natural process for clues to new energy conversion strategies.

In this Account, we will draw on our recent experiments in artificial photosynthetic fuel production in order to illustrate a few general approaches that may be useful for eventually overcoming the energy problem.

Natural Photosynthesis: A Brief Overview

In a chemical context, a fuel is a reduced material that can be oxidized, usually with molecular oxygen, to yield useful energy. Production of a fuel therefore requires a source of energy (e.g., sunlight), a material that can be oxidized to pro-

duce electrons, and a material that can be reduced by those electrons to yield a fuel. On a massive scale such as that required to fill humanity's energy needs, the most viable source of electrons is water oxidation, which also produces oxygen and hydrogen ions. Convenient materials for reduction are the protons from water oxidation to make hydrogen gas, or carbon dioxide to make carbon fuels. Green plants, algae, and cyanobacteria use exactly this approach: energy from the sun is used to oxidize water, and the resulting electrons are at sufficiently negative redox potential to be employed for fuel generation. This can be carbohydrate (useful to humans for direct combustion or ethanol production), lipid (useful for biodiesel production), or even hydrogen gas. Plants carry out conversion by energetically coupling several subsystems. Antenna systems are tuned to gather light efficiently at wavelengths available in the environment of the organism and transfer the resulting excitation energy to reaction centers. They also contain photoprotective mechanisms and regulate the rate of delivery of excitation energy to reaction centers. Reaction centers are nanoscale photovoltaics, using excitation energy to transfer electrons from donors to acceptors, thereby creating energetic charge-separated states that resist recombination long enough to allow migration of the oxidizing and reducing equivalents to catalytic sites for water oxidation and fuel production. The catalytic site for water oxidation is basically identical for all organisms studied to date and is closely coupled to the oxidizing side of the reaction center. The reducing equivalents are transported by redox couples and ultimately used to generate transmembrane proton gradients and synthesize adenosine triphosphate (ATP, a biological energy carrier that is used by many enzymes) and to synthesize the biological two-electron reducing agent β-nicotinamide adenine dinucleotide phosphate (NADPH). The entire system is tuned energetically so that all steps after light absorption are exergonic but still preserve sufficient redox potential, and tuned kinetically so that catalysts are driven at optimal rates and buildup of reactive (and dangerous) intermediates is prevented. Photosynthesis is highly regulated and includes protective mechanisms to limit damage from excess light. Successful photosynthesis thus requires not only carefully "engineered" catalysts and charge separation units but also careful systems engineering. Artificial photosynthetic systems face similar requirements.

Artificial Photosynthesis

Following the biological blueprint, an artificial photosynthetic fuel production system requires antenna/reaction center complexes to harvest sunlight and generate electrochemical poten-
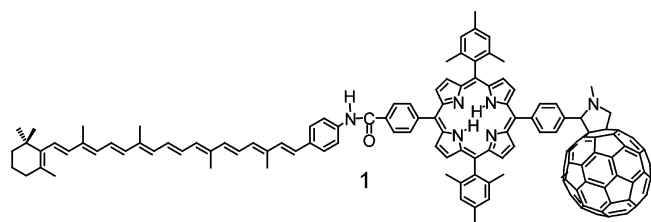
FIGURE 1. Structure of carotenoid−porphyrin−fullerene artificial reaction center **1**.

tial, catalysts for oxidation of water or other electron sources, and catalysts for reduction of precursors to hydrogen or reduced carbon. Although practical systems do not yet exist, considerable progress has been made in the development of the necessary components, and the process of functionally linking these components is under study. We will examine a few illustrative approaches drawn mainly from our research.

Artificial Reaction Centers

Since the late 1970s, many approaches to molecule-based artificial reaction centers have been reported.[1−8] Simple electron donor−acceptor dyads for photoinduced charge separation are relatively easily prepared, and their study has revealed much concerning the basic principles governing electron transfer. However, temporal stabilization of the charge-separated state so that it is kinetically competent to carry out redox reactions with catalysts or other species generally requires at least a three-component (triad) system. Carotenoid (C)−porphyrin (P)−fullerene (C_{60}) molecular triad **1** illustrates the function of such a system (Figure 1).[9]

The triad can be thought of as a molecular photovoltaic. Its function has been examined using transient spectroscopic methods. In 2-methyltetrahydrofuran solution, excitation of the porphyrin yields the first excited singlet state $C-^1P-C_{60}$, which decays by photoinduced electron transfer to the fullerene with a time constant τ of 32 ps. This gives $C-P^{\bullet+}-C_{60}^{\bullet-}$ with a quantum yield of 0.99. At this stage, the molecule has converted light to electrochemical potential, but charge recombination of $C-P^{\bullet+}-C_{60}^{\bullet-}$ to yield the ground state, wasting the stored energy as heat, occurs with $\tau = 3.3$ ns. Such a short lifetime would make accessing the redox potential challenging. In the triad, however, a rapid shift of the positive charge to the carotene (hole transfer, $\tau = 125$ ps) competes effectively with charge recombination, yielding $C^{\bullet+}-P-C_{60}^{\bullet-}$ with an overall quantum yield of 0.95. This final charge-separated state has a lifetime of 57 ns. A closely related $C-P-C_{60}$ triad has a lifetime for charge separation of 170 ns at ambient temperatures and ∼1 μs at 77 K.[10]

Each electron transfer step in the triad occurs rapidly enough to compete with loss of energy by other pathways because it possesses sufficient thermodynamic driving force, and the electronic coupling between the initial and final states is relatively strong. However, the charges in the final $C^{\bullet+}-P-C_{60}^{\bullet-}$ state are spatially well-separated and coupling is weak, so that recombination is slow even in the face of a large driving force (>1.0 eV). Stepwise recombination is slow because the first step is endergonic. This strategy for achieving a long-lived, energetic charge-separated state in high yield via sequential rapid, short-range electron transfers is also employed by natural reaction centers. We initially used this approach[11,12] in 1983, and many artificial reaction centers employing the idea have subsequently been reported.

Antenna/Reaction Center Complexes

Most of the sunlight used for photosynthesis is not absorbed by reaction centers but rather by antenna systems that transfer the resulting singlet excitation energy to reaction centers. The use of antennas is dictated in part by the photophysics of chlorophylls. Chlorophylls are universally used as the primary excited state electron donors in reaction centers. Chlorophyll *a* has very strong light absorption around 430 and 660 nm but relatively weak absorption bands in the visible region between these wavelengths. Photosynthetic organisms have accessory antenna chromophores to harvest energy in regions where chlorophyll is not effective. These commonly include carotenoid polyenes and in some cases phycoerythrins and phycocyanins. A wide variety of antenna morphologies and compositions are found in nature, as might be expected from the wide variety of light conditions under which photosynthesis occurs. All antennas feature strong absorption by multiple chromophores, extremely rapid singlet−singlet energy transfer among chromophores (to compete with relaxation of excited states by other mechanisms), and rapid energy transfer to reaction center chlorophylls.
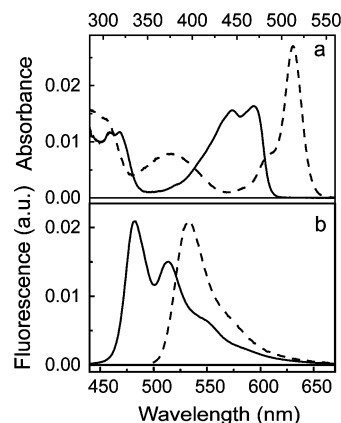
Artificial photosynthetic systems can benefit from antenna systems as well. The primary electron donors in artificial reaction centers do not absorb equally at all wavelengths, and antennas can increase the overall efficiency of collection of solar radiation. Antennas can also absorb light over a relatively large area and deliver excitation energy to a single reaction center, where the electrochemical potential generated may be accessed and utilized. Antennas can also incorporate photoprotective mechanisms.[13−15] Artificial antennas that use various architectures have been reported. Although many of these are based on arrays of porphyrins or other cyclic tetrapyrroles,[16−22] some include other chromophores. The designers of artificial anten-
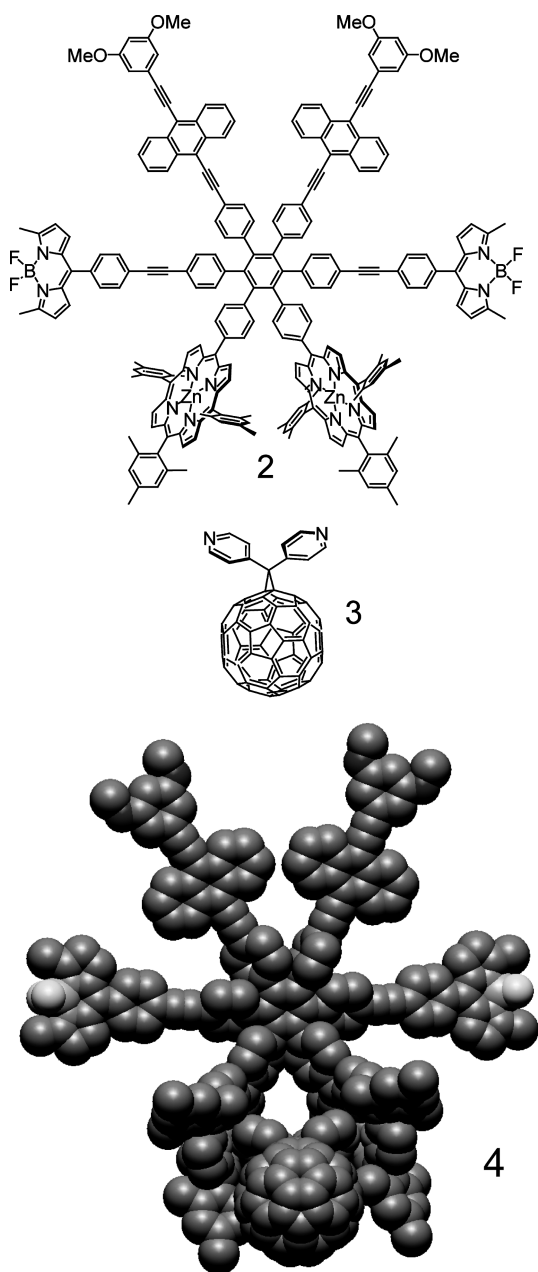
FIGURE 2. Multichromophoric hexad antenna **2** self-assembles with dipyridylfullerene electron acceptor **3** to form antenna/reaction center complex **4**.

FIGURE 3. Absorption (a) and fluorescence emission ($\lambda_{ex} = 400$ nm) (b) spectra of model BPEA (solid) and model BDPY (dashed) chromophores in 2-methyltetrahydrofuran.

nas aim to achieve strong absorption throughout the visible and rapid, efficient energy transfer among the chromophores. In addition, a successful antenna must be capable of interfacing to an artificial reaction center so that singlet energy transfer to the reaction center is also efficient. At the same time, it should not interfere with the electron transfer processes that occur in the reaction center.

Molecular hexad[23] **2** (Figure 2) is a recent example of an artificial antenna whose design evolved from related but simpler systems.[24] The three light-absorbing components are bis(phenylethynyl)anthracene (BPEA), borondipyrromethene

(BDPY), and zinc tetraarylporphyrin (P). The BPEA absorbs strongly in the blue region of the spectrum around 450 nm (Figure 3a), wavelengths at which the porphyrin has almost no absorption. The BDPY has its absorption maximum in the green, at 513 nm. Neither the porphyrin nor BPEA absorb strongly there. The porphyrin has strong absorption in the Soret region at 418 nm and at orange and red wavelengths, with two major Q-bands at 557 and 598 nm. Thus, the three different kinds of chromophores span the visible spectral region from the blue to red wavelengths around 600 nm, and hexad **2** has the potential to harvest sunlight throughout this region. However, to be effective, the antenna chromophores must rapidly transfer excitation energy among themselves and ultimately to a charge-separation unit. One requirement for rapid transfer is thermodynamic; transfer must be exergonic or energy-neutral. The fluorescence emission spectra of model BPEA and BDPY chromophores are shown in Figure 3b. The BPEA emission overlaps well with the absorption of the BDPY, a requirement for singlet–singlet energy transfer. Likewise, the emission of BDPY overlaps well with the porphyrin absorption band at 557 nm. The molecule is poised thermodynamically to funnel excitation energy from BPEA to BDPY, and on to the zinc porphyrin.

Efficient energy transfer must compete with decay of excited states by internal conversion, intersystem crossing, fluorescence, and other decay pathways that limit singlet excited state lifetimes to a few ns or less for molecules of these types (2.80 ns for BPEA and 260 ps for BDPY). Energy transfer by the commonly observed Förster mechanism[25] depends strongly upon the distance separating the two chromophores and their relative orientation, in addition to various excited state properties. Hexad **2** was designed so that the relatively rigid hexaphenylbenzene core serves to con-
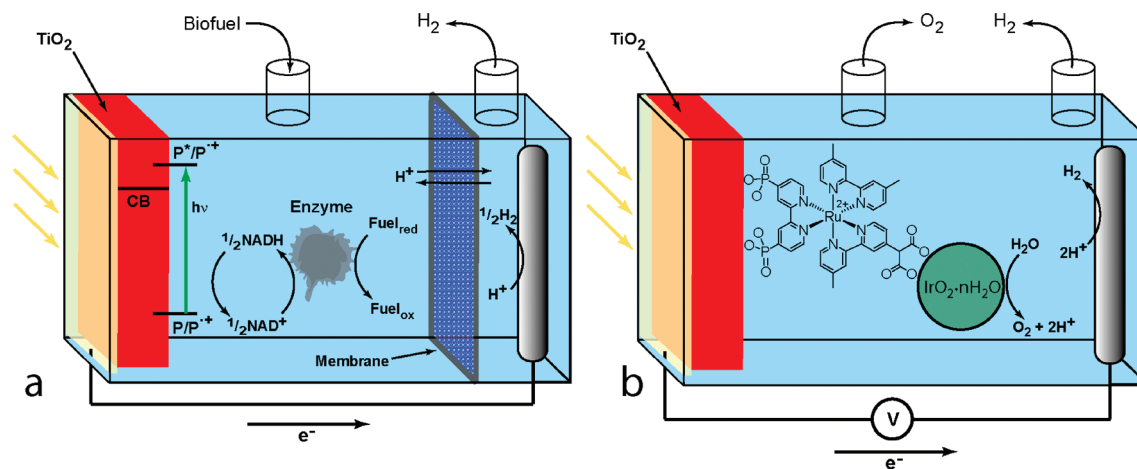
FIGURE 4. Schematic diagrams of a photoelectrochemical biofuel cell (a) and an artificial photosynthetic water splitting cell (b). Both cells use light to generate hydrogen.

strain the chromophores to locations suitable for rapid energy transfer. Transient studies on **2** and model compounds in 1,2-difluorobenzene show that excitation of a BPEA is followed by energy transfer between the two BPEA units with a time constant τ of 400 fs. Energy is then transferred to BDPY with $\tau \leq 13$ ps. The BDPY excited state moves the excitation to the porphyrin with $\tau \leq 15$ ps, generating the porphyrin first excited singlet state. In addition to this stepwise energy transfer sequence, BPEA can transfer excitation directly to the porphyrins with $\tau = 6-7$ ps. These energy transfer steps all work together to generate the porphyrin first excited singlet state with a quantum yield close to unity.

Hexad **2** was coupled to a charge-separation unit by mixing it with fullerene electron-acceptor **3**. The two pyridyl groups of **3** coordinate with the zinc atoms in the porphyrins of **2** to yield heptad **4**. The heptad functions as an antenna/reaction center complex. Transient studies show that the fullerene accepts an electron from a porphyrin excited state with $\tau = 3$ ps to generate $P^{\bullet+}-C_{60}^{\bullet-}$ with a quantum yield of unity. Due to the strong interaction between the fullerene and porphyrins, the lifetime of the charge-separated state is rather short (230 ps).

Photosynthesis requires manipulation of highly energetic redox carriers by inherently reactive complex biomolecules. For this reason, it incorporates extensive photoprotective and regulatory mechanisms to limit photodamage. It is likely that artificial photosynthetic systems will also require protection and regulation if they are to be durable enough to serve practical purposes. Exploration of this aspect of artificial photosynthesis has begun. For example, carotenoid polyenes provide photoprotection from singlet oxygen damage by quenching the precursor chlorophyll triplet states, and take part in the nonphotochemical quenching (NPQ) regulatory mechanism

found in plants. These roles of carotenoids have been investigated in artificial systems.[26,27] In addition, an artificial photosynthetic antenna/reaction center system that is capable of self-downregulation in bright light has been reported.[14]

Generation of a Solar Fuel

As illustrated above, it is possible to design and construct artificial antenna/reaction center complexes that do a creditable job of collecting solar energy and converting it to electrochemical potential. How can this potential, residing within a molecule, be used to generate a fuel? There are many approaches to this problem. For example, we have previously reported a system that uses an artificial reaction center to generate biologically useful energy stored in transmembrane proton gradients and ATP.[28,29] Here, we will describe one pathway for production of a technologically useful fuel, hydrogen, that, while not currently practical, demonstrates that solar fuel production by artificial photosynthesis is possible.

Photoreforming Biofuels to Hydrogen

A step toward solar fuel production via artificial photosynthesis is the photoelectrochemical cell shown in Figure 4a, which uses sunlight to consume a biofuel such as glucose, ethanol, or methanol and generate hydrogen gas.[30−32] The photoactive component is the anode, which is related to those of dye-sensitized nanoparticulate wide band gap semiconductor cells for electricity production.[33] The anode is glass covered with a transparent conductor such as indium tin oxide (ITO) or fluorinated tin oxide (FTO). A thin layer of nanoparticulate SnO_2 or TiO_2 is sintered onto the conductor. The nanoparticles are covered with a self-assembled layer of 5-(4-carboxyphenyl)-10,15,20-tris(4-methylphenyl)porphyrin sensitizer, and the resulting electrode is immersed in a buffered aqueous solu-

tion containing NADH (β-nicotinamide adenine dinucleotide)/ NAD$^+$ (or alternatively NADPH/NADP$^+$). Upon illumination of the anode, the porphyrins absorb light and their excited singlet states relax by rapid electron injection into the nanoparticulate metal oxide, generating P$^{•+}$. Electrons from the anode flow through a wire to the cathode, which is immersed in the same buffer solution and separated from the anode compartment by an ion-selective membrane that allows hydrogen ions to diffuse throughout the solution. The cathode bears a hydrogen producing catalyst such as platinum or a natural hydrogenase enzyme. If oxygen is present at the cathode, it can be reduced by a platinum electrode, and the cell produces electricity rather than hydrogen.

The porphyrin radical cations produced on the photoanode are reduced by NAD(P)H to regenerate the porphyrin ground state and, after a net two-electron transfer process, NAD(P)$^+$. The role of the NAD(P)H is that of an electron relay. The NAD(P)$^+$ is regenerated by reduction by a dehydrogenase enzymatic catalyst for which the NAD(P)H/NAD(P)$^+$ couple is a natural coenzyme. Concurrently, the dehydrogenase oxidizes the appropriate biofuel.

Thus, the cell functions to reform the biofuel to hydrogen. The electrons to reduce H$^+$ come from oxidation of the biofuel, and the electrochemical potential energy to carry out the conversion is provided in part by sunlight. Using this photoanode and suitable enzymes, methanol was oxidized in three two-electron steps to CO$_2$, ethanol was oxidized in two two-electron steps to acetate, and glucose-6-phosphate was oxidized to CO$_2$ and ribulose-5-phosphate.

The use of the NAD(P)H/NAD(P)$^+$ couple is key for the function of the photoelectrochemical biofuel cell, not only because it is required as a coenzyme but also because of its interactions with the sensitized photoanode. This is illustrated by experiments in which either NADH or 1,4-hydroquinone was employed as a sacrificial electron donor.[34] In a cell with the TiO$_2$ photoanode poised at 0 V versus SCE, the maximum photocurrent obtainable with NADH was four times that found using hydroquinone. In related experiments, the photoanode was found to operate at significantly lower potentials with NADH/NAD$^+$ than with the hydroquinone/quinone couple. With 10 mM NADH as the electron donor, increasing the concentration of NAD$^+$ from 0 to 50 mM had little effect on the cell photocurrent, but in a similar experiment with hydroquinone/quinone (H$_2$Q/Q), the photocurrent decreased drastically as the concentration of Q was increased, becoming nearly zero at 10 mM.

These experiments suggest different mechanisms of action for the two redox couples. In the case of QH$_2$, the one-elec-
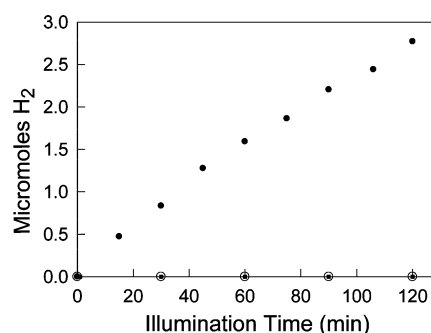
FIGURE 5. Hydrogen production at the Pt cathode of a photoelectrochemical biofuel cell under irradiation with visible light (●). The aqueous buffer contained NAD$^+$, glucose dehydrogenase, and glucose. In the absence of enzyme (■) or glucose (○), no hydrogen was produced.

tron oxidation by P$^{•+}$ at pH = 6 leads to formation of the semiquinone radical (Q$^•$), which can undergo a one-electron oxidation to yield Q. However, from a thermodynamic point of view, both Q (E_m = 0.58 V versus NHE)[35] and Q$^•$ (E_m = 0.10 V)[35] are competent to accept an electron from the conduction band of TiO$_2$ ($\sim$ −0.51 V versus NHE at pH = 6).[36] The results suggest that this occurs readily, and that these charge recombination reactions are responsible for the reduced performance of the cell with the hydroquinone/quinone couple.

In the case of NADH/NAD$^+$, the single-electron oxidation of NADH produces the NADH$^{•+}$ radical ion. This radical is very unstable, and it rapidly deprotonates at pH = 8. The NAD$^•$ radical is also unstable and can readily decay by disproportionation to form NADH and NAD$^+$, dimerization followed by oxidation of the dimer, or in principle electron donation to P$^{•+}$ or electron donation to the TiO$_2$ conduction band. The TiO$_2$ conduction band electrons ($\sim$−0.63 V versus NHE at pH = 8)[36] are not thermodynamically competent to carry out the reduction of NAD$^+$ (−0.92 V versus NHE),[37] and charge recombination at the photoanode is strongly disfavored. Thus, the initial product of NADH oxidation rapidly converts to the inactive NAD$^+$. With the recombination reaction to the redox couple reduced, the cell based on NAD(P)H/NAD(P)$^+$ would be expected to produce larger photocurrents and photovoltages that would be independent of the NAD$^+$ concentration, as observed.

Turning now to the cathode, Figure 5 shows hydrogen production by the cell using a porphyrin-sensitized TiO$_2$ photoanode and a cathode consisting of platinum particles supported on microporous carbon.[31] The photoanode compartment (buffered at pH = 8) contained NAD$^+$, glucose, and glucose dehydrogenase from *Bacillus megaterium*. Illumination with visible light produced hydrogen, which was analyzed gas chromatographically. The NADH concentration increased during the

first few minutes of cell operation and then remained constant for the remainder of the experiment, demonstrating that the source of electrons for hydrogen production was indeed glucose, and not simply NADH. With irradiation at 520 nm, the quantum yield of electron flow was ∼5%, and the quantum yield of hydrogen was therefore ∼2.5%.

The photoelectrochemical biofuel cell successfully uses light to reform biofuel to hydrogen gas, although the yields are low. The light is necessary to provide energy for the process. There is little or no thermodynamic driving force for conversion of the biofuels investigated to hydrogen under the conditions of the experiment, and energy for overpotentials (activation energy) must be supplied as well. The cell has been investigated using a mixture of ethanol and acetaldehyde as the fuel source and with the cathode under 1 atm of hydrogen. Although hydrogen production in the dark is endergonic under these conditions ($E_{cell} \cong -0.18$ V), the illuminated cell produces hydrogen, demonstrating that some fraction of the light energy is conserved as chemical potential in the product.

Although platinum is a good catalyst for electrochemical hydrogen production, it is expensive and of limited availability. Catalysts based on earth-abundant elements are preferable for large-scale solar fuel production. Many organisms produce hydrogen gas enzymatically using iron or iron and nickel in the active site. For example, *Clostridium acetobutylicum* produces the hydrogenase *Ca*HydA, which is a soluble 65.4 kD protein containing a [6Fe-6S] H-cluster active site.[38] It bears additional iron−sulfur sites that are thought to transfer electrons from external carriers to the active site for proton reduction. The enzyme converts hydrogen ions to molecular hydrogen with high specificity and turnover rate, but is inhibited by oxygen. When *Ca*HydA is adsorbed onto a carbon felt cathode in the TiO₂-based photoelectrochemical biofuel cell and the cell is illuminated, hydrogen is produced.[32] The cell operates with little or no overpotential due to the *Ca*HydA, and it demonstrates current densities about equal to those obtained in the same cell with a platinum foil cathode. These results suggest that enzymatic catalysts for hydrogen production can perform comparably to platinum with the advantage of using earth-abundant elements, but the overall stability and oxygen sensitivity of these Fe−Fe hydrogenases would greatly limit their usefulness in solar water splitting. Hydrogenases with greater oxygen stability, either natural or the result of genetic manipulation, would help overcome this problem.

Although the results discussed above demonstrate that conduction band electrons from nanoparticulate TiO₂ are capable of proton reduction, the thermodynamic driving force is not large. Consequently, small changes in energetics can have a large effect on electron transfer rates and hence on efficiency. An example is the effect of hydrogen accumulation at the cathode on performance. Although the cell is able to pressurize hydrogen in excess of two atmospheres, efficiency decreases dramatically as the hydrogen "back pressure" is increased. In a cell operating such that the photocurrent is 40 µA at low H₂ partial pressure, increasing the H₂ pressure to 2.0 atm decreases the photocurrent to about 15 µA.[39] Increasing the hydrogen partial pressure shifts the Nernstian potential of the H⁺/H₂ couple, which, in effect, applies more negative bias to the photoanode. This leads to increased electron density in the conduction band and sub-band-gap states of the TiO₂ film, which in turn gives rise to more charge recombination between these electrons and P•⁺ and oxidized species in solution, thus decreasing efficiency.

Water Splitting via Artificial Photosynthesis

Even if the drawbacks of the photoelectrochemical biofuel cell were overcome, the system would still be far from ideal for practical solar energy conversion. Most of the energy stored in the hydrogen gas was originally solar energy stored in biomass, and the extra stored potential energy provided by the light activating the cell is relatively minor. In addition, the cell produces oxidized carbon as a byproduct, and energy conversion systems based on it or any other biofuel are at best carbon neutral. As mentioned earlier, water is the ideal source of electrons for solar fuel production. The architecture of the photoelectrochemical biofuel cell has recently been employed to oxidize water and produce hydrogen using sunlight, as discussed below.

The modified cell reported by Mallouk and co-workers,[40] diagrammed schematically in Figure 4b, replaces the biofuel oxidation catalyst with a water oxidation catalyst, nanoparticulate IrO₂·*n*H₂O. The nanoparticulate TiO₂ photoanode is sensitized by a ruthenium polypyridyl dye rather than a porphyrin. One of the bipyridine groups chelating the ruthenium bears phosphonates, selective for binding to TiO₂, while a second bears a malonate moiety, selective for IrO₂·*n*H₂O. The photoanode is wired to a platinum catalyst for proton reduction, and both are immersed in aqueous buffer at pH = 5.75. Provision is made for application of an external bias potential.

The principle of operation is similar to that of the photoelectrochemical biofuel cell. Irradiation of the ruthenium sensitizer is followed by electron injection by the sensitizer MLCT state into TiO₂. The injected electrons are conducted through the wire to the cathode, where protons are reduced to hydrogen. The oxidized ruthenium dye is reduced by the iridium oxide nanoparticles, regenerating the sensitizer and accumulating the oxidation
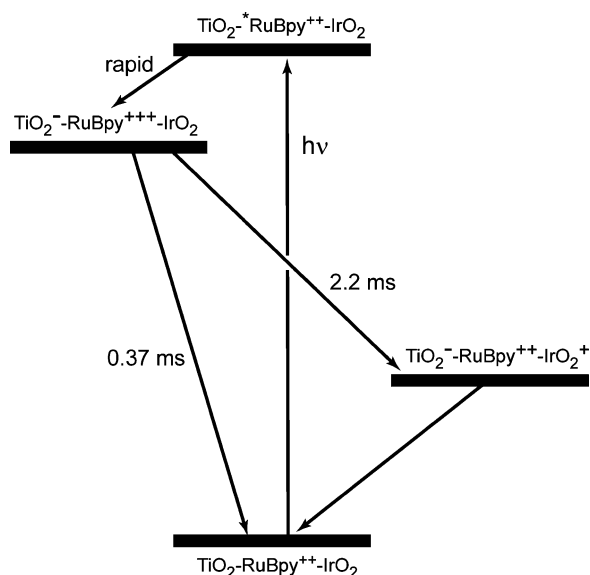
FIGURE 6. Photochemical relaxation pathways for the ruthenium sensitizer in the photochemical water splitting cell. The vertical direction represents energy, but only relative energetics are implied.

potential on the nanoparticle necessary for water oxidation to O_2 and hydrogen ions. The net result is solar production of hydrogen gas and molecular oxygen. In a typical experiment, the photoanode was illuminated with visible light (>410 nm). When a bias of a few hundred millivolts was applied, photocurrent was observed, and the production of hydrogen and oxygen at the cathode and anode, respectively, were confirmed by gas chromatography. Irradiation at 450 nm with an intensity of 7.8 mW/cm^2 of an electrode with $A_{464} = 0.67$ produced a current of 12.7 μA/cm^2, corresponding to a quantum yield of $\sim$0.9%. The cell current gradually decreased over a period of $\sim$4 h. This decrease was accompanied by a bleaching of the sensitizer absorption spectrum, and it is ascribed to destruction of the oxidized dye by nucleophilic attack.

Figure 6 summarizes the results of transient spectroscopic studies of model systems which shed light on the reasons for the low water splitting efficiency. When sensitizer/$IrO_2 \cdot nH_2O$ nanoparticle conjugates in aqueous solution containing the sacrificial electron acceptor $S_2O_8^{2-}$ were illuminated, electron transfer from the excited ruthenium complex to the acceptor was observed, with the formation of the oxidized sensitizer. The $IrO_2 \cdot nH_2O$ donates an electron to the oxidized sensitizer with $\tau = 2.2$ ms, regenerating the ground state of the ruthenium complex. When the ruthenium complex/$IrO_2 \cdot nH_2O$ colloid was adsorbed onto TiO$_2$ nanoparticles in solution and the system illuminated, rapid electron injection from the sensitizer into the TiO$_2$ occurred to yield the oxidized ruthenium complex. Charge recombination from the TiO$_2$ conduction

band to the sensitizer to give the ruthenium ground state was observed with a lifetime of $\sim$0.37 ms.

The results in Figure 6 reveal that a major reason for the low quantum yield of water splitting is that electron transfer from TiO$_2$ to the oxidized sensitizer dye is about 1 order of magnitude more rapid than electron transfer from $IrO_2 \cdot nH_2O$ to the oxidized sensitizer. Charge recombination dominates over oxidation of the water oxidation catalyst and the accompanying electron injection into the circuit for hydrogen production. The same factor doubtless contributes to the requirement for an applied bias for hydrogen production. As the bias is increased, electron flow to produce H$_2$ reduces the electron population in the TiO$_2$ conduction band and associated sub-band-gap trap sites on the TiO$_2$ nanoparticles, reducing the rate of reduction of the oxidized ruthenium sensitizer by recombination. This increases the production of oxidized $IrO_2 \cdot nH_2O$ nanoparticles poised for water oxidation.

The above interpretation is consistent with the results described earlier for the photoelectrochemical biofuel cell. In that case, increasing hydrogen pressure at the cathode led to an increase in the number of electrons in the TiO$_2$ conduction band and trap states, and therefore an increase in the rate of charge recombination at the photoanode and decreased hydrogen production. In other words, in the water-oxidizing cell, recombination from the sub-band-gap states in the TiO$_2$ photoanode draws down the potential of the anode so that H$_2$ production requires added bias. As explained above, recombination in the photoelectrochemical biofuel cell is limited by the electrochemistry of the NADH/NAD$^+$ mediator so that the TiO$_2$ sub-band-gap states "fill up", resulting in sufficiently negative potentials to produce H$_2$ at the cathode without added bias.

This solar water splitting cell is clearly inefficient and too unstable to be useful for practical solar fuel production. In addition, the scarcity of iridium makes it very unlikely that iridium-based catalysts could play a role in solar fuel production on a large scale. Nevertheless, the system does illustrate that hydrogen production via water oxidation can be achieved using ideas drawn from natural photosynthesis and molecular photochemistry.

Conclusions

This Account illustrates that it is possible to employ the tools of chemistry, biochemistry, and materials science and the fundamental principles underlying photosynthetic energy conversion to design and build artificial photosynthetic systems that use sunlight to generate fuels. The photosynthetic blueprint works, as indeed it must, because biology and technology are ruled by the same natural laws. However, artificial

photosynthetic systems in general require dramatic improvements in efficiency and durability before they can be considered for practical application. This is a great challenge, but one that must be met.

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