

Approaches for biological and biomimetic energy conversion

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This article highlights areas of research at the interface of nanotechnology, the physical sciences, and biology that are related to energy conversion: specifically, those related to photovoltaic applications. Although much ongoing work is seeking to understand basic processes of photosynthesis and chemical conversion, such as light harvesting, electron transfer, and ion transport, application of this knowledge to the development of fully synthetic and/or hybrid devices is still in its infancy. To develop systems that produce energy in an efficient manner, it is important both to understand the biological mechanisms of energy flow for optimization of primary structure and to appreciate the roles of architecture and assembly. Whether devices are completely synthetic and mimic biological processes or devices use natural biomolecules, much of the research for future power systems will happen at the intersection of disciplines.

biotechnology | nanotechnology | photosynthesis | photovoltaic

Recently, the National Academies and the Keck Foundation held a meeting to discuss the development of new applications for nanotechnology[¶] with the goal of identifying challenges where the convergence of nanoscience and physical and biosciences could provide a revolutionary outcome. One area clearly in need of new technologies is biological and biomimetic methods of energy conversion. Within this broad area, focus was given to two specific applications: the conversion of solar energy into useful electrical or chemical energy and the production of power for *in vivo* medical devices. The following sections will provide both an economic perspective on current photovoltaic (PV) technology and an overview of the various research efforts toward using or mimicking biological systems to improve current and future energy-conversion systems.

Consumption, Economic Drives, and Technological Needs

The total energy consumption in the United States in 2004 was 99.74 quadrillion Btu (British thermal units) (1.05×10^{20} J), and this value has been increasing at a rate of $\approx 1.4\%$ per year since the early 1980s. Currently, $\approx 22\%$ of the energy is provided by coal, $\approx 23\%$ from natural gas, 37% from petroleum (excluding alcohol), 8.2% from nuclear power, 2.7% from hydroelectric sources, and 2.8% from wood, waste, and alcohol. Solar energy accounts for $<0.1\%$ (1).

The average solar radiation available for a flat-plate collector in the U.S. is $5 \text{ kW}\cdot\text{h}/\text{m}^2$ per day ($1 \text{ kW}\cdot\text{h} = 3.6 \times 10^6 \text{ J}$). Conservatively, 100 million residences, each with an available roof area of 90 m^2 , receive $\approx 5 \times 10^{19} \text{ J}$ of solar energy, which is equal to half of the an-

nual energy consumption in the U.S. Typical commercially available PV cells offer nominal efficiencies of $\approx 15\%$, with higher levels attainable up to a theoretical efficiency for silicon PV cells of 32% ; however, a significant fraction of the installation costs are related to infrastructure, such as supporting framework, wiring, power inverters, and grid connections. For example, in a study published in 2003 of a 35-kW PV array (2), the total reported cost was \$239,945 ($\$6.86/\text{W}$), with infrastructure comprising $35\text{--}40\%$ of the total amount. This system saved \$2,678 per year in energy costs compared with the preinstallation expenditures. If, hypothetically, the same installation could be made with cells at $1/10$ the current price and 32% efficiency but the same infrastructure costs, the system would cost $\approx \$100,000$ and save $\approx \$8,000$ per year. Based on these values, it is apparent that improving efficiency and reducing device costs is vital to using PV technologies but that addressing infrastructure costs will also be necessary.

The losses in energy conversion associated with the fundamental behavior of silicon can be overcome by using alternative materials and structures, some of which may be designed to mimic natural biological processes. Although direct solar-to-hydrogen conversion methods may prevent some of the losses associated with fully photosynthetic systems (see below), they are limited by a thermodynamic efficiency of $13\text{--}15\%$ (3). More recent calculations suggest that this limit may be higher for terrestrial systems under special circumstances [for example, the energy needed to hydrolyze water can be reduced by using waste heat and appropriate photosensitizers and catalysts (4)], but the losses

associated with storing and transporting the hydrogen and in converting it into electricity still remain.

The following sections of this paper will focus on materials and devices that use synthetic and/or hybrid approaches to mimic natural photosynthetic energy-conversion processes.

Biological Energy Production

Photosynthesis. Photosynthesis involves a complex set of reactions that start with the absorption of a photon. The resulting energy can be converted into ATP or fed into a light-independent process that results, in the presence of chlorophyll, in the conversion of carbon dioxide and water into carbohydrate, oxygen, and water. Oxygenic photosynthesis also results in the production of oxygen and is used by plants, algae, and oxyphotobacteria. Anoxygenic photosynthesis occurs in simpler organisms, such as green and purple photosynthetic bacteria, and produces a carbohydrate, a reduced acid, and water from carbon dioxide and molecules such as hydrogen sulfide or an organic acid, which serve as electron sources.

The energy absorption and transduc-

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Abbreviations: PV, photovoltaic; PSI, photosystem I.

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tion scheme depends on both spatial and molecular configurations. The reaction center is a protein complex in which photon energy is converted to an electrochemical potential in the form of charge separation across a membrane. The primary electron donor is either chlorophyll or bacteriochlorophyll, and the electron receptor is bacteriochlorophyll (type I) or bacteriopheophytin (type II). In type-I reactions, the electron travels from an iron-sulfur complex in the reaction center to other iron-sulfur molecules and finally into ferredoxin, a water-soluble protein that can be transported away from the membrane. In type-II reactions, the electron is passed to a quinone electron acceptor and then to a second quinone. When this second quinone receives another electron (from a separate reaction), it forms a quinol, which can be carried away by diffusion.

Photon capture and energy transfer to the reaction center are highly dependent on an antenna structure that acts as a light harvester to increase the frequency and effective cross section for absorption. Spontaneous absorption of a photon has been estimated to happen at a rate of 1.7×10^{-2} to 1.7×10^{-3} per s (5). There is a practical limit to antenna molecule size; calculations based on either energy-transfer times or hopping kinetics result in a limit for antenna size of ≈ 200 chromophores (5).

The electron donor for each reaction in photosynthesis can be characterized by the energy of the photon that is used: photosystem I (PSI) functions at 700 nm (1.77 eV) ($1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$), photosystem II functions at 680 nm (1.82 eV), green sulfur bacteria function at 840 nm (1.48 eV), and green nonsulfur bacteria function at 870 nm (1.43 eV). For comparison, the high-energy photons in the UV region have energies in the range of 3.10–4.28 eV. The difference in energy between the absorbed photon and the electron donor is lost as heat, just as the excess energy is lost when a high-energy photon is absorbed by a silicon PV cell. Most plants are not able to deal with the excess energy of UV photons and often do not absorb them at all. If these high-energy photons were absorbed, they might reduce the genetic stability of the plant's genome (6), destroy the light-harvesting complex (7), or induce apoptotic-like (programmed cell death) changes (8). Photons of lower energies are also not used for photosynthesis. It is possible to calculate the energy efficiency of green plants, given the spectral distribution of light at the Earth's surface; the net energy has been shown to have an upper bound of 9.2% (9). Because some of this

energy is consumed by the plant, a maximum net efficiency of $\approx 5\%$ is commonly reported (9–11).

Summarizing the sources of energy losses in natural photosynthetic processes provides a means to prioritize synthetic efforts (12): 47% of the energy from the available incident solar radiation is lost because the energy falls outside of the range that is used. Thirty percent of the absorbed energy is lost to incomplete absorption or absorption that does not feed the photosynthesis process. Twenty-four percent of the useable absorbed energy is wasted because of the degradation to the energy level that can be processed by the photosystems. Sixty-eight percent of the remaining energy is used to create chemical energy in the form of glucose. Finally, in an ideal system, 30–40% of the glucose is used by the plant for its natural processes.

Light-Driven Proton Pumps. Bacteriorhodopsin has been recognized as one of a few natural light-driven proton pumps (13, 14). After absorbing photon(s), these proteins cycle through a series of intermediate conformations that result in a proton being transported to the outside of the cell. Purified halorhodopsin has been shown to change its transport mechanism as a function of the wavelength of incident light, from a single-photon chloride transporter to a two-photon proton pump (15). Site-specific mutants of bacteriorhodopsin were able to reproduce this behavior (16), showing that the ion specificity can be designed. Functional bacteriorhodopsin has also been transfected into naturally nonphotoactive organisms (17, 18), introducing the possibility of producing specialized organisms that are optimized for solar energy conversion.

Opportunities for Nanotechnology: Synthetic and Biomimetic Approaches for Solar Energy Conversion

Using Biological Systems. Artificial systems to mimic photosynthesis have been fabricated by self-assembling heterolayers of proteins. One approach has been to layer photochromic proteins such as GFP with organic molecules such as viologen through Langmuir-Blodgett techniques (19). Similarly, a protein-based photodiode was fabricated by using layer-by-layer assembly of cytochrome *c* and GFP onto gold substrates. The cytochrome *c* was covalently tethered to the gold surface, and GFP was chemisorbed onto the cytochrome *c* layer (20); the device produced reproducible photocurrents with repeated on/off cycles. Photosynthetic reaction centers from purple bacterium have been

incorporated into devices by self-assembling them using polyhistidine tagging of gold-indium tin oxide surfaces and stabilizing them with surfactant peptides before coating with a protective organic semiconductor layer (21).

Bacteriorhodopsin and other light-driven proton pumps have also been used to generate photocurrents as isolated proteins. Some of the earliest work (16) found that surfaces coated with the protein could produce a transient signal similar in behavior to normal photoreceptors; this phenomena has been shown to function at a variety of electrolyte/electrode interfaces (22, 23). Although these findings were quickly extended into efforts to make artificial retinas (24) and protein-based optical storage devices (25–29), issues of interfacing the proteins with conventional semiconductors led to the development of synthetic or modified bacteriorhodopsin devices using organic cations.^{||}

PSI has been used recently as an optical trigger for a retinal prosthesis (31). The concept was based on previous work on retinal prosthesis in which patterned electrical stimuli were shown to elicit visual perceptions (32). The isolated PSI reaction centers were able to produce $>1 \text{ V}$, which is sufficient to trigger neural responses. The ability to reconstitute plant proteins into mammalian cells to mimic physiological function provides an interesting glimpse at the potential for future hybrid systems.

For many protein-based devices, harnessing the natural energy-transfer process for devices requires that the molecules be patterned with specific directional and spatial orientation (33, 34). There has been much work done to develop methods to assemble both bacteriorhodopsin and PSI into oriented, two-dimensional arrays (35, 36). Bacteriorhodopsin has the capability of assembling *in vitro* into stable, well ordered two-dimensional arrays (28). Koyama *et al.* (33) used antibodies to mediate the orientation of purple membrane monolayers and demonstrated that the greatest photocurrent was observed when the cytoplasmic side of the purple membranes was directed to the electrode, with opposite and random orientations producing the weakest and intermediate values, respectively. Similar to the bacteriorhodopsin work, Greenbaum and coworkers (34) found that self-assembling PSI on organosulfur-modified gold substrates imparted stability in laboratory experiments and

^{||}Birge, R. R., Chen, Z., Govender, D. S. K., Stuart, J. A., Tallent, J. R., & Tan, E. H. L., 212th ACS National Meeting, Aug. 25–29, 1996, Orlando, FL, p. PHYS-123.

for long-term storage. By controlling the directionality of PSI, electrostatic potentials of single PSI reaction centers could be measured through Kelvin force probe microscopy under dark–light illumination (34).

Fully and Partially Synthetic Systems: Artificial Photosynthesis. Efforts to mimic natural photosynthetic processes have been under way since 1912, when Giacomo Ciamician (37) envisioned artificial photosynthesis to be “the photochemistry of the future.” Considerable progress has been made both to understand the molecular mechanisms of photosynthesis and to develop synthetic and engineering methods to extend the biological processes to synthetic systems (38–40). In the last 20 years, there have been significant efforts to synthesize and engineer artificial light-harvesting antennae and reaction centers, and a wide variety of donor and acceptor molecules and macromolecular architectures have been produced and characterized (41, 42). Recently, the advent of nanotechnology has provided a wealth of materials (nanoparticles, nanowires, carbon nanotubes, fullerenes, etc.) that exhibit novel physical, chemical, and optical characteristics that can be harnessed to improve existing methods of energy transduction (43–46).

In almost all cases, whether the devices are composed of natural biomolecules or synthetic organic or inorganic molecules, the architecture and spatial arrangements at multiple length scales have proven to play a pivotal role (39, 41, 47). Although it is very difficult to reproduce the dynamic physics of biological self-assembly outside of living systems, applying similar noncovalent chemistries and using traditional engineering methods to produce well ordered systems have been shown to be plausible methods for producing artificial photosynthesis (40, 48–50).

In photosynthesis reaction centers, photo-induced energy flow is controlled through a series of spatially arranged chromophores that are electronically coupled to produce a gradient such that energy is transferred from absorbed photons to the reaction center. Because spatial precision is critical to this energy-transfer process, extensive work has explored the synthesis and characterization of modular architectures where photoactive components are linked together covalently in a precise manner (20, 41, 42, 51–53). The ability to couple donor and acceptor molecules covalently allows one to overcome the limitations of diffusion. It also allows one to probe systematically how chain architecture, distance between donor and acceptor,

and differences in their energy levels affect energy transfer and charge separation.

One of the earliest architectures synthesized and probed was molecular dyads where multiple types of chromophores were linked into linear, one-dimensional chains. Dimers composed of porphyrin or chlorophyll were first shown to mimic the reaction center special pair (BChl *b*) (54, 55). The dimers were followed by molecular dyads consisting of a carotenoid polyene and chlorophyll to mimic the properties of the light-harvesting antenna (38, 51, 56), because the carotenoid increases the solar absorption cross section of chlorophyll and transfers excitation energy to the chlorophyll.

A significant challenge for artificial photosynthesis is the ability to achieve long-lived charge separation and prevent charge recombination (41, 52, 57, 58). One way to address this challenge has been to integrate successive energy gradients into covalently linked molecular dyads that will quickly shuttle electrons away from the excitation site to more stable sites. A molecular triad made up of carotene, porphyrin, and naphthoquinone (C-P-Q) demonstrated photoinduced charge separation that could be stabilized up to several microseconds (59). A molecular linear pentad consisting of carotenoid-polyene-metallated (Zn) porphyrin-freebase porphyrin-diquinone [C-P_{Zn}-P-Q_A-Q_B] has been shown to perform efficient photoinduced electron transfer and produce a charge-stabilized state with an overall quantum yield of 0.83 and a lifetime of 55 s. The molecular order of the pentad was critical for charge stabilization because it was constructed such that all of the possible electron transfer pathways would converge to the same final charge-separated structure (60). Much of this work has recently been extended using fullerenes (C₆₀) as the electron acceptors; examples include triads such as a porphyrin-bearing fullerene covalently linked to a carotenoid polyene (41, 57, 61–65).

Electron transfer properties of molecular wires, in which donor and acceptor molecules are covalently linked by molecular bridges (donor–bridge–acceptor, DBA), have also been studied as model systems for short-range energy transfer (53, 66). Although the electronic structure of these systems typically limits the distances over which efficient charge separation can occur, Wasielewski, Ratner, and coworkers (53) reported in 1998 a set of tetracene (donor) pyromellitimide (acceptor) DBA molecules with nearly distance-independent electron transfer. Their results emphasize the

importance of energy matching between donor and acceptor molecules to achieve efficient energy transfer, even at distances as large as 40 Å.

Light-harvesting and energy-transfer properties of linear photoactive polymer systems have also been investigated (67–69). In some of the earliest work, a trapping molecule was attached to the polymer backbone, and the effect of trap sensitization through excitation of the main polymer chromophore was studied (70). One of the major difficulties of using linear polymeric systems, however, is that light harvesting and directional energy migration are impeded by polymer chain folding, especially in response to solvent, temperature, and arrangement of pendant groups (52, 71). Because of these issues, rigid, shape-persistent macromolecules such as dendritic systems may provide certain advantages over linear architectures (52).

Since their introduction by Tomalia *et al.* (72) and Newkome *et al.* (73) in 1985, many dendrimers have been synthesized and investigated (74). The wheel-like and spherical structures of multiporphyrin and dendrimer arrays provide a scaffold for attaining directional energy transfer, allowing excitation energy to cascade efficiently from the periphery to the core. Furthermore, the highly branched nature of dendrimers and multiporphyrin wheels allows coupling of more than one donor moiety per acceptor moiety that can be used to increase the molar absorptivity (52, 75–78). Building blocks for these structures have included transition metal complexes (ML_n), metal-free and metal-chelated porphyrin groups, and various other conjugated photoactive units (20, 42, 52, 76, 77, 79). Jiang and Aida (80) synthesized dendrimers from aryl ethers with a photoisomerizable azobenzene core and demonstrated that a five-generation azobenzene dendrimer could photoisomerize upon infrared excitation. Their work leads to the possibility of using such materials to harvest and channel low-energy photons for chemical transformations.

Natural photosynthesis depends on energy flow between noncovalently assembled chromophores. Noncovalent self-assembly techniques are being developed for synthetic photoactive devices (48, 50, 81–83). Although some of the materials are self-organized through chemical interactions to produce larger scale arrays, others are organized on surfaces by using techniques such as Langmuir–Blodgett films or synthesized by assembling encapsulated materials into or onto host–guest inorganic matrices. Wasielewski *et al.* (47, 84) recently reported that xanthene-linked green

chromophores tetrafunctionalized with perylene-bis(dicarboximide) were highly efficient at both light harvesting and ultrafast charge separation. The researchers attributed this efficiency to the molecules' ability to self-assemble into stacked arrays with defined orientations between adjacent planar aromatic groups (47, 84). Self-assembled monolayers of carotenoids and chlorophylls on titania surfaces showed long-lived photoinduced charge separation due to a reductive quenching of the pheophytin molecules upon pheophytin excitation at 670 nm (81). The stable charge separation was proposed to be due to either the conjugated backbone of the carotenoid-polyene, which withdraws positive charges from the tetrapyrrole, or to positive charge-hopping between the aggregated carotenoids. As mentioned earlier, nanostructured inorganic matrices have also been used to direct and spatially confine the orientation of multichromophore systems. Calzaferrri *et al.* (50) used zeolites as a host material and inserted various dyes and electron acceptors into the nanometer channels, using either gas-phase or ion exchange techniques. The narrow channels confined the molecules to form single, linear, one-dimensional molecular chains within each pore. The mutual orientations of the encapsulated dyes ensured efficient energy-transfer processes whether energies were injected from or into the stopper molecules that capped the ends of the dye-loaded channels.

Similar to the photoisomerization work described earlier (80), much re-

search has focused on increasing the absorption cross section of new materials by capturing both the high- and low-energy photons that are normally lost. One approach is to use all of the available energy of high-energy photons by generating multiple excitons from a single absorbed photon. Ellingson *et al.* (85) reported multiple exciton generation by using PbSe and PbS quantum dots; Qi *et al.* (86) have also reported similar results with polymer-quantum dot blends (86). The ability to capture and use all of the energy from a high-energy photon greatly improves the overall energy efficiency of solar energy conversion. Related work in optical storage and imaging with two-photon (87, 88) and three-photon (30) absorption could provide the materials and methods to use the energy from low-energy photons to provide a means to capture the lower energy tail of the solar spectra not currently being used.

A large number of materials have been developed that can harvest photons and efficiently transfer the energy to moieties that stably separate charged species (the basis of an electrical potential). Coupling these materials and devices into full systems for power generation has been much more challenging. Moore and coworkers (40) demonstrated the feasibility of coupling light harvesting with the generation of chemical potential energy: one of the few examples of a system built completely from synthetic constituents. Their system was based on self-assembled liposomes containing both the

C-P-Q (carotene-porphyrin-naphthoquinone) molecular triad and CF₀F₁-ATP synthase. When the liposomes were irradiated at 633 nm, they produced ATP by a proton gradient that formed across the lipid bilayer through redox reactions between the embedded C-P-Q triad and the lipophilic quinone.

Conclusions

Although an enormous amount of research has been conducted to develop biological and biomimetic methods for energy production, significant challenges remain. One grand challenge that remains is to transfer the high level of performance seen in laboratory-based photoactive reactions and systems into commercial devices. Harnessing solar power with biological or biomimetic systems is clearly an activity that would benefit from multidisciplinary efforts. There is a great need for those who work at the molecular and atomic levels to collaborate with those who best understand the physical properties and engineering of complex systems. The era of nanotechnology, especially the bridging of the disparate fields, offers opportunities to challenge the conventional wisdom regarding the efficiency and cost effectiveness of alternative energy sources.

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