

REPORTS OF THE PANELS ON BASIC RESEARCH NEEDS FOR SOLAR ENERGY UTILIZATION

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BASIC RESEARCH CHALLENGES FOR SOLAR ELECTRICITY

CURRENT STATUS

Edmund Becquerel discovered the photovoltaic (PV) effect in 1839, when he observed that a voltage and a current were produced when a silver chloride electrode immersed in an electrolytic solution and connected to a counter metal electrode was illuminated with white light (Becquerel 1839). However, the birth of the modern era of PV solar cells occurred in 1954, when D. Chapin, C. Fuller, and G. Pearson at Bell Labs demonstrated solar cells based on p-n junctions in single-crystal Si with efficiencies of 5–6% (Chapin, Fuller, and Pearson 1954). This original Si solar cell still works today — single-crystal Si solar cells dominate the commercial PV market.

From the mid 1950s to the early 1970s, PV research and development (R&D) was directed primarily toward space applications and satellite power. Then, in 1973, a greatly increased level of R&D on solar cells was initiated following the oil embargo in that year, which caused widespread concern regarding energy supply. In 1976, the U.S. Department of Energy (DOE), along with its Photovoltaics Program, was created. DOE, as well as many other international organizations, began funding PV R&D at appreciable levels, and a terrestrial solar cell industry quickly evolved. Figure 1 shows a plot of annual PV power production vs. time for the period 1988–2003 (Surek 2005). Total global PV (or solar) cell production increased from less than 10 MW_p/yr in 1980 to about 1,200 MW_p/yr in 2004; the current total global PV installed capacity is about 3 GW_p. The “peak watt” (W_p) rating is the power (in watts) produced by a solar module illuminated under the following standard conditions: 1,000 W/m² intensity, 25°C ambient temperature, and a spectrum that relates to sunlight that has passed through the atmosphere when the sun is at a 42° elevation from the horizon (defined as air mass [or AM] 1.5;

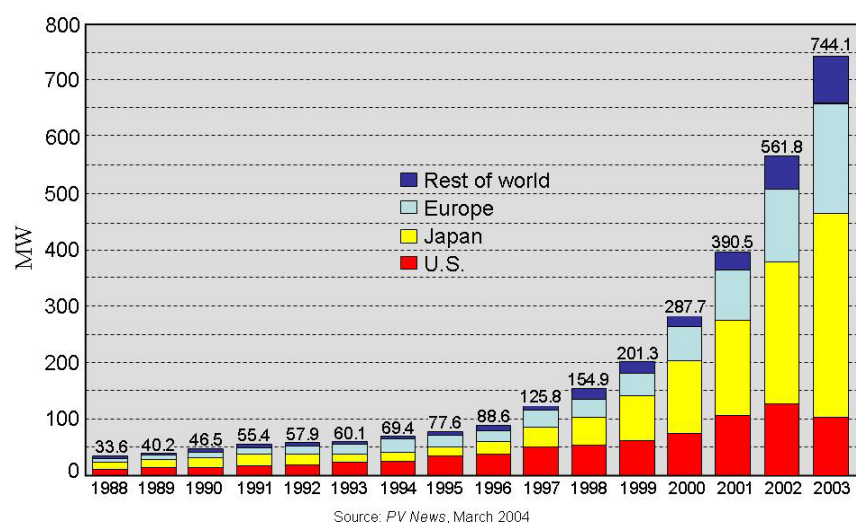
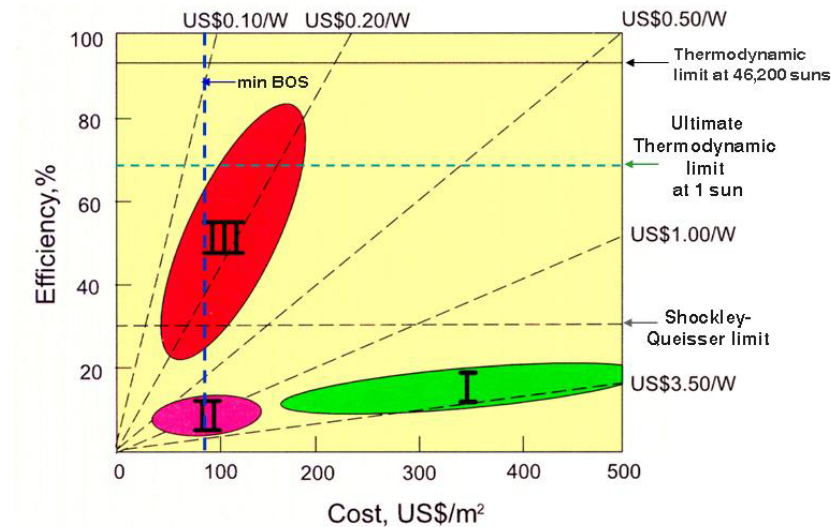


Figure 1 World PV cell/module production (in MW_p)

i.e., when the path through the atmosphere is 1.5 times that when the sun is at high noon). Because of day/night and time-of-day variations in insolation and cloud cover, the average electrical power produced by a solar cell over a year is about 20% of its W_p rating.

Solar cells have a lifetime of approximately 30 yr. They incur no fuel expenses, but they do involve a capital cost. The cost for the electricity produced by the cell is calculated by amortizing the capital cost over the lifetime of the cell and considering the total electrical output energy produced over the cell lifetime. Higher PV efficiency thus directly impacts the overall electricity cost, because higher-efficiency cells will produce more electrical energy per unit of cell area over the cell lifetime. The cost figure of merit for PV cell modules ($\$/W_p$) is determined by the ratio of the module cost per unit of area ($\$/m^2$) divided by the maximum amount of electric power delivered per unit of area (module efficiency multiplied by $1,000 \text{ W/m}^2$, the peak insolation power). In Figure 2, this cost per peak watt ($\$/W_p$) is indicated by a series of dashed straight lines having different slopes. Any combination of areal cost and efficiency that is on a given dashed line produces the same cost per peak watt indicated by the line labels. Present single-crystalline Si PV cells, with an efficiency of 10% and a cost of $\$350/m^2$, thus have a module cost of $\$3.50/W_p$. The area labeled I in Figure 2 represents the first generation (Generation I) of solar cells and covers the range of module costs and efficiencies for these cells.

In addition to module costs, a PV system also has costs associated with the non-photoactive parts of the system. These are called balance of system (BOS) costs, and they are currently in the range of $\$250/m^2$ for Generation I cells. Thus, the total cost of present PV systems is about $\$6/W_p$. Taking into account the cost of capital funds, interest rates, depreciation, system lifetime, and the available annual solar irradiance integrated over the year (i.e., considering the diurnal



For PV or PEC to provide the full level of C-free energy required for electricity and fuel—solar power cost needs to be ~2 cents/kWh ($\$0.40/W_p$).

Figure 2 PV power costs ($\$/W_p$) as function of module efficiency and areal cost (Source: Green 2004)

CONVERSION OF SUNLIGHT INTO ELECTRICITY

Solar power can be converted directly into electrical power in photovoltaic (PV) cells, commonly called solar cells. The sun has a surface temperature of about 6,000°C, and its hot gases at this temperature emit light that has a spectrum ranging from the ultraviolet, through the visible, into the infrared.

According to quantum theory, light can behave either as waves or as particles, depending upon the specific interaction of light with matter; this phenomenon is called the wave-particle duality of light. In the particle description, light consists of discrete particle-like packets of energy called photons. Sunlight contains photons with energies that reflect the sun's surface temperature; in energy units of electron volts (eV), the solar photons range in energy ($h\nu$) from about 3.5 eV (ultraviolet region) to 0.5 eV (infrared region). The energy of the visible region ranges from 3.0 eV (violet) to 1.8 eV (red); the peak power of the sun occurs in the yellow region of the visible region, at about 2.5 eV. At high noon on a cloudless day, the surface of the Earth receives 1,000 watts of solar power per square meter (1 kW/m²).

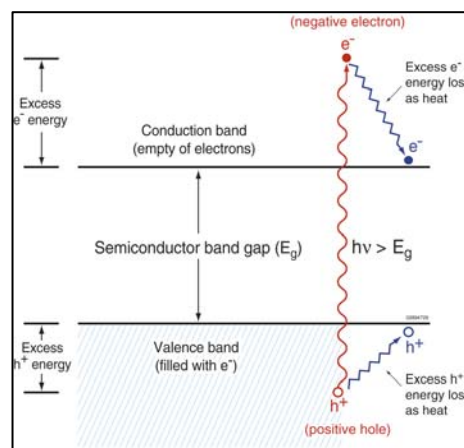
Photovoltaic cells generally consist of a light absorber that will only absorb solar photons above a certain minimum photon energy. This minimum threshold energy is called the "energy gap" or "band gap" (E_g); photons with energies below the band gap pass through the absorber, while photons with energies above the band gap are absorbed. The light absorber in PV cells can be either inorganic semiconductors, organic molecular structures, or a combination of both.

In inorganic semiconductor materials, such as Si, electrons (e^-) have energies that fall within certain energy ranges, called bands. The energy ranges, or bands, have energy gaps between them. The band containing electrons with the highest energies is called the valence band. The next band of possible electron energies is called the conduction band; the lowest electron energy in the conduction band is separated from the highest energy in the valence band by the band gap. When all the electrons in the absorber are in their lowest energy state, they fill up the valence band, and the conduction band is empty of electrons. This is the usual situation in the dark.

When photons are absorbed, they transfer their energy to electrons in the filled valence band and promote these electrons to higher energy states in the empty conduction band. There are no energy states between the valence and conduction bands, which is why this separation is called a band gap and why only photons with energies above the band gap can cause the transfer of electrons from the lower-energy-state valence band into the higher-energy-state conduction band. When photons transfer electrons across the band gap, they create negative charges in the conduction band and leave behind positive charges in the valence band; these positive charges are called holes (h^+). Thus, absorbed photons in semiconductors create pairs of negative electrons and positive holes. In a PV cell, the electrons and holes formed upon absorption of light separate and move to opposite sides of the cell structure, where they are collected and pass through wires connected to the cell to produce a current and a voltage — thus generating electrical power.

In organic molecular structures, the energy of the photons also must first exceed a certain threshold to be absorbed. This absorption creates an energetic state of the molecular system, called an excited state. These excited molecular states can also generate separated electrons and holes.

Furthermore, certain organic polymers and other molecular structures can form organic semiconductors that provide the basis for organic PV devices. One difference between inorganic and organic PV cells is that in organic cells, the electrons and holes are initially bound to each other in pairs called excitons; these excitons must be broken apart in order to separate the electrons and holes to generate electricity. In inorganic PV cells, the electrons and holes created by the absorption of light are not bound together and are free to move independently in the semiconductor.

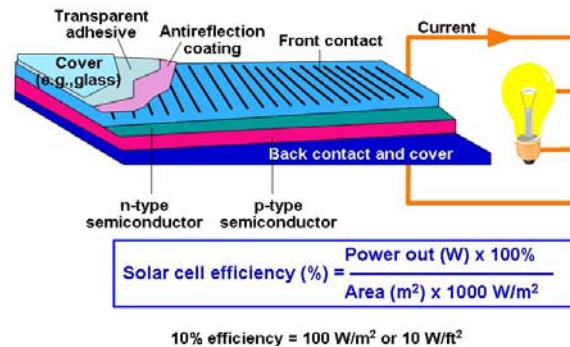


TYPES OF PHOTOVOLTAIC CELLS

All PV cells depend upon the absorption of light, the subsequent formation and spatial separation of electrons and holes, and the collection of the electrons and holes at different energies (called electrical potential). The efficiency of electron and hole formation, separation, and collection determines the photocurrent, and the energy difference between the electrons and holes in their final state before leaving the cell determines the photovoltage. The product of the photocurrent and photovoltage is the electrical power generated; this product, divided by the incident solar irradiant power, determines the efficiency of converting solar power to electrical power. The output power rating of a solar cell is expressed as the peak power (W_p) generated at high noon on a cloudless day.

PV cells can be divided into three categories: (1) inorganic cells, based on solid-state inorganic semiconductors; (2) organic cells, based on organic semiconductors; and (3) photoelectrochemical (PEC) cells, based on interfaces between semiconductors and molecules. The figure shows the structure of an inorganic solar cell based on a sandwich structure of two types of semiconductor material: one type has mobile free negative electrons (called an n-type semiconductor), and the second type has mobile free positive holes (called a p-type semiconductor). The sandwich, called a p-n junction, allows the photogenerated electrons and holes to be separated and transferred to external wires for electrical power production. PV cells have no moving parts and are silent. (Source: Surek 2005)

A Solar Cell Structure



cycle and cloud cover, which produces an average power over a year that is about 1/5 of the peak power rating), the $\$/W_p$ cost figure of merit can be converted to $\$/\text{kWh}$ by the following simple relationship: $\$/W_p \sim \$0.05/\text{kWh}$. This calculation leads to a present cost for grid-connected PV electricity of about $\$0.30/\text{kWh}$. Areas labeled II and III in Figure 2 present the module costs for Generation II (thin-film PV) and Generation III (advanced future structures) PV cells.

Figure 3 presents the historical progress of the best reported solar cell efficiencies to date (Surek 2005). The efficiencies of commercial (or even the best prototype) modules are only about 50–65% of the efficiency of the best research cells. The plot includes the various PV technologies of single-crystal Si, thin films, multiple-junction cells, and emerging technologies — such as dye-sensitized nanocrystalline TiO_2 cells and cells based on organic compounds.

Over the past decades, improvements have also been made in a second important metric, the manufacturing cost of PV modules. The prices of PV modules have followed a historical trend along a so-called “80% learning curve.” That is, for every doubling of the total cumulative production of PV modules worldwide, the price has dropped by approximately 20%. This trend is illustrated in Figure 4 (Surek 2005). These data are based on annual surveys conducted by PV

PHYSICS OF PHOTOVOLTAIC CELLS

Inorganic PV and electrochemical PV (EPV) cells operate upon the establishment of an electric potential difference between the n- and p-type regions in an inorganic PV cell or between an n- or p-type semiconductor and redox electrolyte, in the case of an EPV cell. This difference creates an electrical diode structure. The current-voltage behavior of such junctions follows the diode equations, in which the current flow in one direction across the junction is constant with voltage, whereas the current flow in the other direction across the junction increases exponentially with the applied voltage. Hence, the dark current density (J_{dark} [amps/cm²]), as a function of the voltage (V) applied to this diode (assuming ideal diode behavior), is:

$$J_{\text{dark}}(V) = J_0(e^{qV/kT} - 1) \quad (1)$$

where J_0 is a constant, q is electronic charge, k is Boltzman's constant, and T is temperature (K).

If a diode is illuminated, additional charge carriers will be created upon absorption of the light. These carriers will create an additional current flow across the junction, and they must be added to the dark current to obtain the total current in the system. For illumination with light comprising many different wavelengths, the total photo-induced current can be calculated by summing (i.e., integrating) the contributions to the current from excitation at each wavelength. Hence, the short-circuit photocurrent density (J_{sc}) is:

$$J_{\text{sc}} = q \int I_s(E) (QY)(E) dE \quad (2)$$

where I_s = solar photon flux, E = photon energy (inversely proportional to the wavelength of the photon), and QY = quantum yield (electrons collected per incident photon).

The net current density (J) is:

$$J(V) = J_{\text{sc}} - J_{\text{dark}}(V) = J_{\text{sc}} - J_0(e^{qV/kT} - 1) \quad (3a)$$

However, ideal diode behavior is seldom seen. This is accounted for by introducing a non-ideality factor, m , into Equation 3a:

$$J(V) = J_{\text{sc}} - J_{\text{dark}}(V) = J_{\text{sc}} - J_0(e^{qV/mkT} - 1) \quad (3b)$$

Because no current flows at open circuit, the open-circuit voltage (V_{oc}) for the ideal device is obtained by setting $J(V) = 0$,

$$V_{\text{oc}} = [kT/q] \ln [(J_{\text{sc}}/J_0) + 1] \quad (4)$$

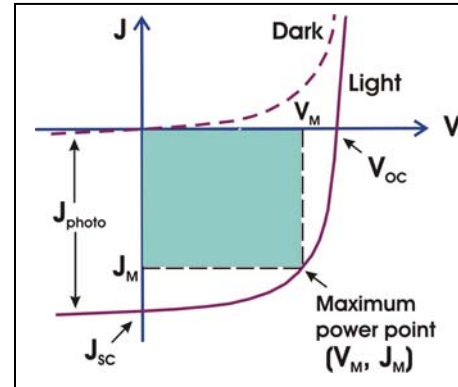
A plot of the net photocurrent density (J) vs. voltage is provided in the figure, which shows the current-voltage characteristic of a PV cell.

The conversion efficiency (η) of the PV cell is determined by the maximum rectangle in the figure that can fit within the net photocurrent-voltage characteristic. The maximum power point of the cell, or so-called operating point, is the values of J and V (J_m and V_m) at which the maximum rectangle in the figure meets the J - V curve. This defines a term called the "fill factor" (FF)

$$FF = J_m V_m / J_{\text{sc}} V_{\text{oc}} \quad (5)$$

that characterizes the "squareness" of the J - V characteristic. The maximum FF value is 1.0; it occurs when $J_m = J_{\text{sc}}$ and $V_m = V_{\text{oc}}$, but in reality, the diode equation limits the maximum FF to 0.83.

The cell conversion efficiency is the electrical power density ($J_m V_m$) (watts/cm²) divided by the incident solar power density (P_{sun}), multiplied by 100 to obtain a percent value.



$$\eta = J_m V_m / P_{\text{sun}} = 100 * J_{\text{sc}} V_{\text{oc}} FF / P_{\text{sun}} \quad (6)$$

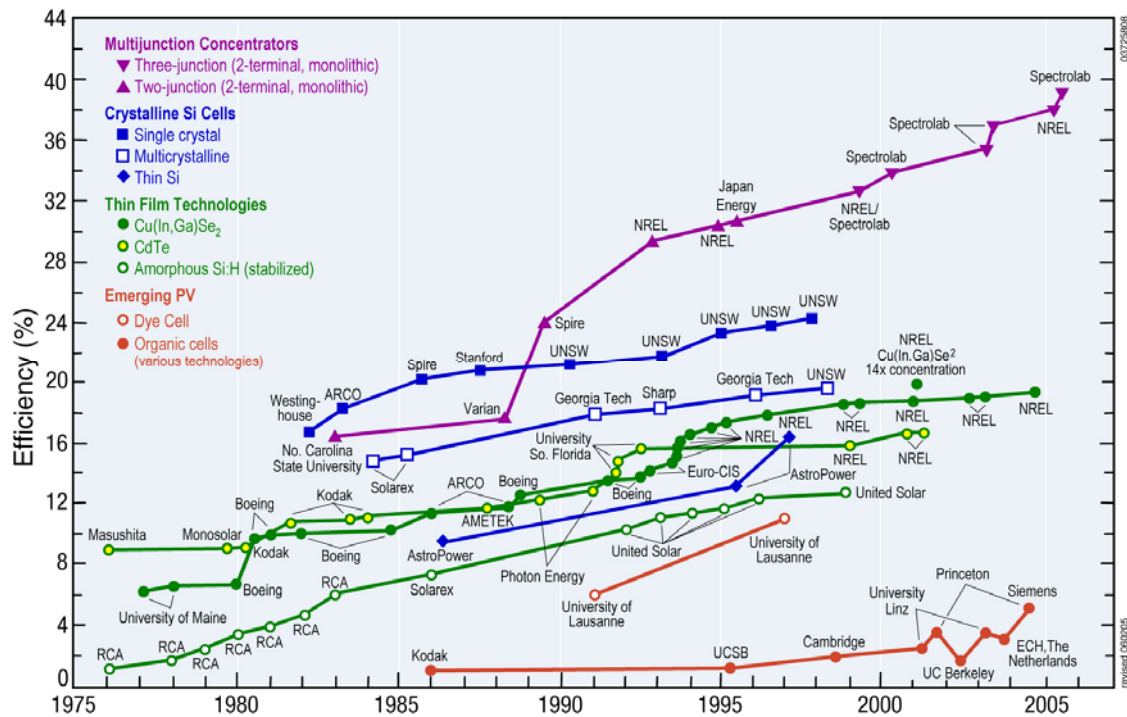


Figure 3 Improvements in solar cell efficiency, by system, from 1976 to 2004

News (PV Energy Systems 2004). The final data point for 2003 corresponds to about \$3.50/W_p and a cumulative PV capacity of 3 GW. An important issue, in terms of future projections, is how this price-reduction trend will continue in the future. As Figure 4 shows, a major reduction in the projected future cost of PV modules depends upon the introduction of thin films, concentrator systems, and new technologies.

The third significant metric for PV cells is module reliability. Today, most crystalline Si module manufacturers offer warranties of 25 years, typically guaranteeing that the power output of the module will not decrease by more than 20% over this period.

Further details about the current status of solar electricity technologies, costs, and implementation can be found in the Solar Electric Technology Assessment in Appendix 1.

IMPACT OF INEXPENSIVE SOLAR ELECTRICITY

In 2004, the United States consumed approximately 4.0×10^{12} kWh (energy consumed in one year at an average power of 0.46 TW) of electricity (Energy Information Administration [EIA] 2005); this amount represents about 14% of total U.S. energy consumption (EIA 2005). The U.S. electricity produced by solar PV cells currently represents a tiny fraction (<0.02%) of the total electricity supply. The challenge for generators of solar electricity is to produce it at very low cost, ultimately approaching \$0.40/W_p, which is equivalent to an energy cost of \$0.02/kWh. Achieving this cost would require a reduction in the \$/W_p price of about a factor of 15–25

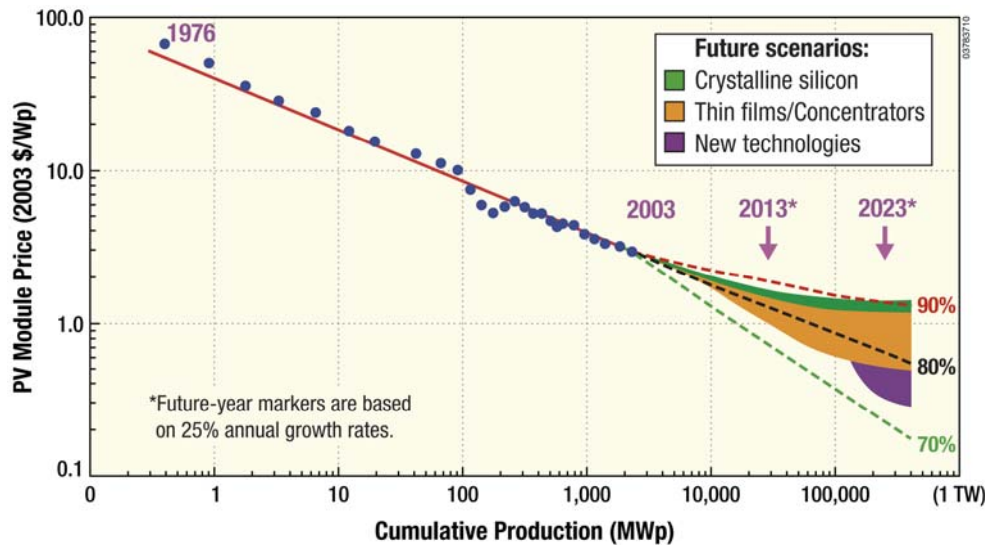


Figure 4 Learning curve for PV production. The present learning curve rate is 80% (20% cost reduction for every doubling of cumulative production); projected rates of 90% and 70% are shown for years beyond 2003. (Source: Surek 2005)

relative to present PV costs. Such a low cost for solar electricity would be expected to result in massive implementation of solar energy systems in the energy infrastructure in the United States and globally. Such a cost breakthrough would also represent a major advance in using solar energy to alleviate the anticipated future problems associated with energy supply, energy security, and unacceptable levels of atmospheric CO₂. In addition to satisfying electrical power needs, solar electricity at \$0.02/kWh could also contribute to the goal of producing cost-effective non-carbonaceous solar fuels, such as hydrogen (National Academy of Engineering, Board on Energy and Environmental Systems 2004). However, to achieve the latter goal, major advances in suitable and scalable storage and distribution technologies will also be required.

Solar electricity can be produced from PV cells or from turbines operating with high-temperature steam produced from concentrated solar power. This Panel Survey addresses only PV solar cells; the latter method for producing solar power is discussed in the section on Basic Research Challenges for Solar Thermal Utilization.

Need for Revolution on Existing Technology Path

Since the 1970s, the PV industry has continually reduced the cost of solar electricity. Over the past three decades, the cost of PV modules has decreased at a rate of 20% for each doubling of module production (see Figure 4). The cost of PV modules per peak watt has declined from about \$70/W_p in 1976 to about \$3.50/W_p in 2003. The BOS cost (support structures, maintenance, land, etc.) for a grid-tied PV system is about \$2.50/W_p. Considering both module and BOS costs, together with present cell efficiencies, the cost of solar electricity has dropped from about \$3.65/kWh in 1976 to about \$0.30/kWh in 2003. However, if the present learning curve for PV cells is followed, the projected attainment of very-low-cost PV power (\$0.02/kWh) and its widespread implementation would lie far in the future (20–25 years depending upon the

annual production growth rate; see Figure 5). Therefore, basic research is needed to not only maintain the existing technology path and learning curve in support of evolution, but to also produce a revolution to dramatically change the slope of the historical learning curve and produce dramatic reductions in the PV module cost-to-efficiency ratio (Figure 5). The goal is to reduce the cost per peak watt by a factor of about 15–25 relative to present systems through the use of new designs, materials, and concepts for solar electricity production, and to do so more quickly than would be accomplished by staying on the existing learning curve — thereby materially impacting global energy supply in 10–15 years rather than by the mid-21st century.

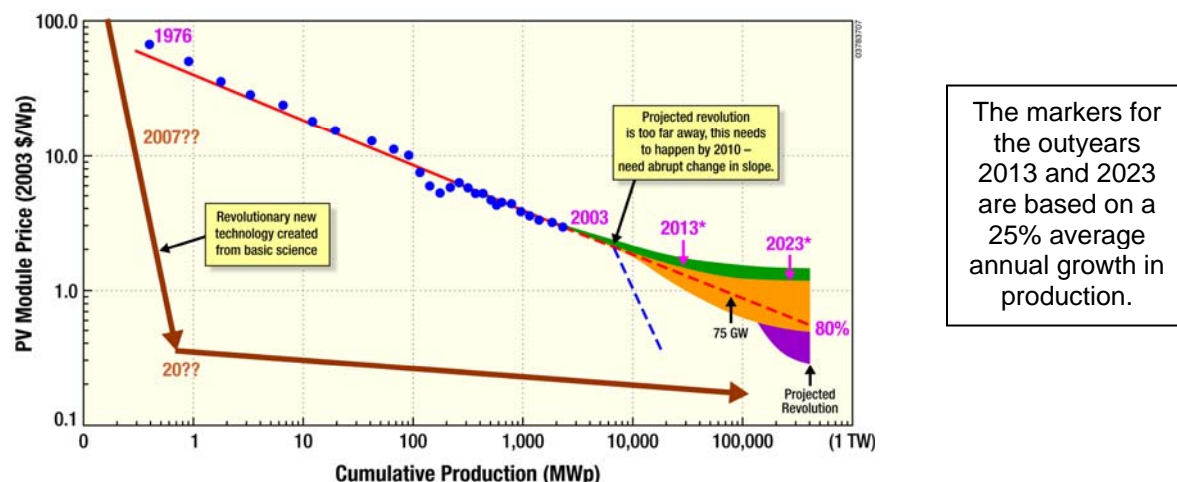


Figure 5 Learning curve for solar cells. The module price has been dropping 20% for every doubling of module production (80% learning curve) since 1976. Extrapolation of this historical trend into the future, plus a projected technological revolution at an annual production level of 150,000 MW_p, results in a prediction that \$0.40/W_p would not be reached for another 20–25 yr. Reaching \$0.40/W_p sooner to accelerate large-scale implementation of PV systems will require an intense effort in basic science to produce a technological revolution that leads to new, as-yet-unknown technology. This revolution requires a major reduction in the ratio of the PV module cost per unit area to the cell efficiency.

The following paragraphs describe the basic research that is required to produce breakthroughs that would change the slope of the learning curve and accelerate cost reduction (Surek 2005).

Needs of the Si Photovoltaic Industry. More than 99% of today's PV production is Si based, with the best performance coming from the highest-quality single crystals and the lowest performance from amorphous Si cells. Because of the inherent costs of making and handling wafers, the production cost would be substantially reduced if high-quality crystals could be obtained by thin-film growth on glass or on another inexpensive substrate. Thin-film crystalline Si on glass is now used for some display technologies. An exciting research opportunity would use this thin-film Si technology to grow high-efficiency solar cells at the cost of amorphous Si cells. Even though Si technology is considered to be relatively mature, planar, one-sun Si cells have recently set new performance records by use of heterointerfaces with amorphous Si to passivate the surfaces and withdraw carriers. Further improvements in performance are presently limited because researchers do not yet understand the mechanisms of this improvement.

Needs of Direct-gap, Thin-film Photovoltaic Technologies. A second strategy for reducing costs is to use thin-film materials that have a very high absorptivity for solar photons. Such materials are called direct-band-gap semiconductors; Si is an indirect-band-gap semiconductor and absorbs relatively weakly, thus requiring a relatively large thickness of Si in the PV cell to absorb all the incident sunlight. Substantial research efforts have produced direct-band-gap CdTe and CuInSe₂ solar cells with efficiencies approaching 20%. Industrial efforts to manufacture cells made of these materials in high volumes are beginning to demonstrate success. However, this process has been slower than expected because much of the basic science of these solar cells is not understood. These polycrystalline solar cells are affected by many things, including the grain structure obtained for growth on foreign substrates, the effects of intentional and unintentional impurities on doping and performance (e.g., injection of sodium affects the performance of CuInSe₂ cells), and the nature of the active junction and ohmic contacts formed by poorly understood processes. A basic understanding of these issues would facilitate the technology transfer to large-scale production, enabling a revolutionary growth of the PV industry.

Needs of Concentrator Cell Technology. A third strategy would reduce costs by using inexpensive optics to concentrate the light on small-area solar cells. Four recent achievements/developments provide a foundation and momentum:

- (1) An efficiency of 37.9% has been obtained, with possible pathways to higher efficiencies.
- (2) Lattice mismatched III-V solar cells with performance approaching the radiative limit have been demonstrated, implying that such cells may reach efficiencies in the 40–50% range.
- (3) A 1-kW multi-junction concentrator system is now supplying electricity to the grid, paving the way for larger prototypes and manufacturing; and
- (4) In 2004, installations with sizes >100 kW increased to 20 MW, implying that a market appropriate for concentrators may be emerging.

Taken together, these recent developments imply that concentrator cell technology may be poised for rapid growth. Key to this growth is the integration of multiple materials for fabrication of higher-efficiency solar cells.

Need for Revolution to Create New Technologies

In addition to investing in basic research to support a slope change in the present evolutionary path of existing PV technologies — including crystalline Si, thin-film approaches, and multiple-junction tandem cells — an aggressive, high-risk research program must be developed for as-yet-unknown or nascent approaches to solar energy conversion. Such a research effort must target the development of inherently high-efficiency and low-cost conversion concepts to rapidly

achieve dramatic improvements in the economics of solar energy. This strategy is illustrated in Figure 5.

BASIC SCIENCE CHALLENGES, OPPORTUNITIES, AND RESEARCH NEEDS IN SOLAR ELECTRICITY

Inorganic Photovoltaics

As shown in Figure 2, single-crystal Si solar cells, defined as Generation I cells, have module efficiencies of about 10–12% — leading to module costs of about \$3.50/W_p. In order to lower the areal cost, Generation II approaches to PV systems involve the use of semiconductor thin films (amorphous Si, polycrystalline CdTe and CuInSe₂, dye cells, and organic PV cells). However, the system cost will be limited by BOS costs, which means that the Generation II systems cannot have arbitrarily low efficiency even if the module costs are negligible. With low areal costs for both modules and BOS of \$75/m² each, 10% efficiency for Generation II modules (17% cell efficiency) would yield PV costs of \$1.50/W_p (\$0.075/kWh). Thus, unless the module and BOS costs can be reduced well beyond the aggressive target of \$75/m² each, achieving the goal of \$0.40/W_p (\$0.02/kWh) will require efficiency and system costs per unit area that lie in the Generation III area of Figure 2.

A critical feature of Generation III PV systems is that their module efficiencies are above 32% — the thermodynamic limit calculated by Shockley and Queisser (1961). In the Shockley-Queisser analysis, a major assumption is that electrons and holes created by absorption of photons with energies above the band gap lose their excess energy (the difference between the photon energy and the semiconductor band gap) as heat through excitation of the lattice vibrations (this is called phonon emission). However, thermodynamic calculations that do not make this assumption show that the thermodynamic efficiency limit can be above 65% if the energetic electrons and holes created by the high-energy photons do not convert the excess energy to heat but produce higher photovoltages or photocurrents (Green 2004; Ross and Nozik 1982; Marti and Luque 2004). Reaching the goals of ultra-high efficiencies and low cost will require basic research to achieve the revolutionary advances indicated in Figure 5.

Another way to achieve efficiencies above the Shockley-Queisser limit is to use a series of semiconductor p-n junctions arranged in a tandem configuration (these cells are called multi-junction solar cells). Of the approaches proposed to achieve higher efficiency, only multi-junction solar cells have been able to actually exceed the performance of conventional single-junction solar cells. Figure 6 shows the current world-record efficiencies (as a function of the number of junctions) compared with the efficiency limit that is predicted by the thermodynamic analyses. At one sun, the single-junction efficiency is about 75% of the theoretical limit; the multi-junction and concentrator cells show even more opportunity for improvement. The thermodynamic limit for solar-energy conversion is significantly higher still: 66% at one sun and 86% at full solar concentration (46,200 suns). The achievement of even higher efficiencies and lower costs for multi-junction solar cells will require basic research to bring about the revolution in existing technology and change the slope of the learning curve, as presented in Figure 5. The

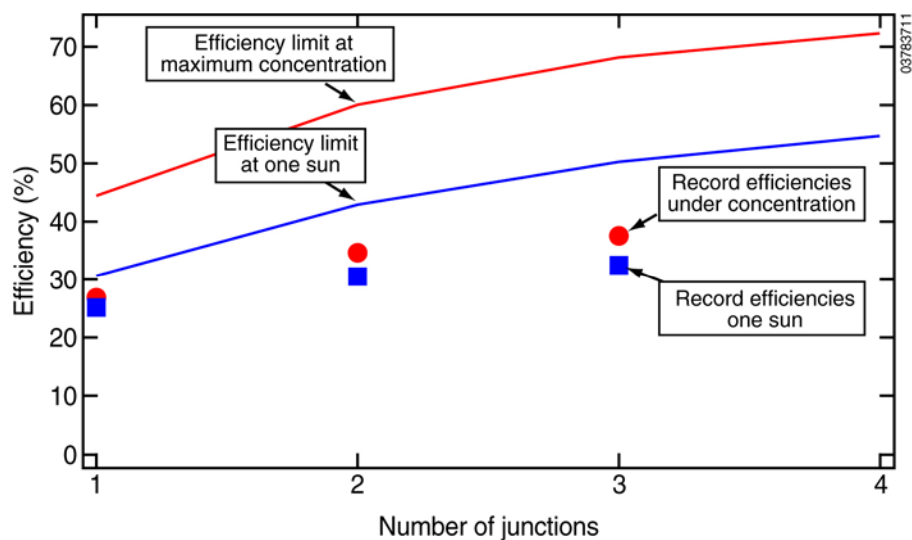


Figure 6 Current record efficiencies (as a function of the number of junctions) compared with the theoretical limits as predicted by the detailed balance analysis

pathway to achieving these higher efficiencies may require identification and exploitation of new phenomena involving photon manipulation, absorption, charge creation, and separation; new materials; and novel device structures — or it may build on the evolution of present-day technologies. The grand challenge is to push solar cell efficiencies toward their theoretical limits while maintaining low cost; this can only be done through fundamental research that identifies new photon phenomena, new materials, and improved implementation of the more familiar materials.

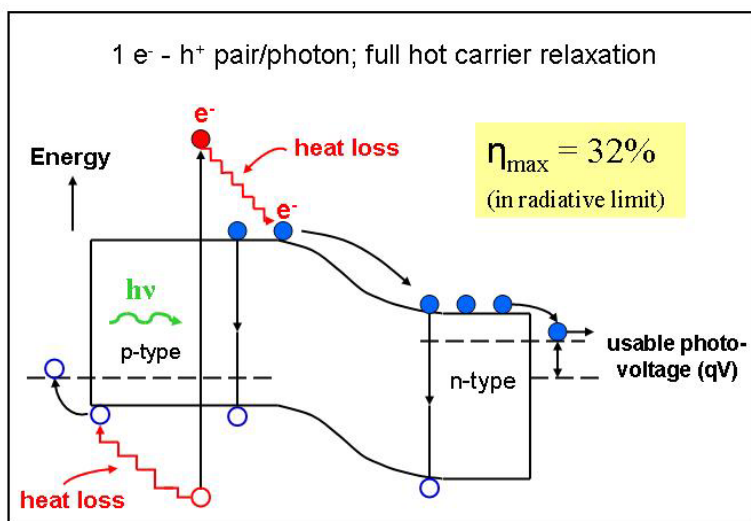
Organic Photovoltaics

Solid-state PV cells based on carbonaceous (organic) matter were first discovered 20 years ago (Tang 1986). Early work on organic photovoltaics using molecular-based systems demonstrated the concept; however energy conversion efficiencies were low. Considerable excitement in this area was generated by a report published in the mid-1990s of 2.9%-efficient cells based on conducting organic polymers mixed with derivatives of C_{60} (fullerene) (Yu et al. 1995). During the past decade, refinements in the chemical components of the cells, improvements in cell physics, and device engineering have led to individual demonstration cells that operate at greater than 5% solar-to-electrical-power conversion efficiency. The opportunities and potential payoff here are significant: low-cost, lightweight, large-area, flexible, high-efficiency solar cells. The materials are basically like those used in video display technology, and they offer the possibility of very significant cost reduction, as well as flexibility in installation, form factor, etc. The basic research goal is to develop sufficient understanding of such materials and structures to improve their conversion efficiency by a factor of 5–10, and thus obtain robust, scalable efficiencies of 15–25% in cheap, plastic-type solar cells (Figure 7).

INORGANIC PV CELLS

Inorganic PV cells are based on solid-state semiconductors, for example Si or GaAs. Very small amounts of impurities (called dopants) are added to the semiconductors to endow them with either extra free and mobile electrons (an n-type semiconductor) or extra free and mobile holes (a p-type semiconductor). When the n-type and p-type semiconductors are joined together, they form what is called a p-n junction, and an electric field is created between the two regions. When the cell is illuminated, and electrons and holes are thus created, this electric field helps to efficiently separate the negative electrons from the positive holes. Two electrical contacts to the cell then provide a path for the electrons to leave the cell; pass through the external circuit to deliver electric power; and then, finally, return to the cell to recombine with the holes to neutralize them and complete the circuit. The semiconductors do not absorb solar photons that have energies lower than the semiconductor band gap; photons with energies higher than the band gap are absorbed, but the extra energy above the band gap is converted to heat rather than to electrical energy. This loss of photon energy to heat is one of the reasons why the calculated maximum efficiency of conventional solar cells is limited to about 32%.

The figure shows a conventional single p-n junction inorganic PV cell.



The basic principle of operation in an organic PV cell is that illumination of a mixture of electron-rich (donor) and electron-poor (acceptor) species leads to separation of (+) and (-) charge carriers. Collection of these carriers at electrodes produces an electrical current that can do work on a load in an external circuit. Although the basic principles behind the operation of organic PV cells and conventional p-n junction cells are similar, the details of key events, such as charge carrier generation and charge transport, are very different in the organic cells. Consequently, the basic understanding of the physics and chemistry of organic PV systems lags behind that of conventional p-n junction

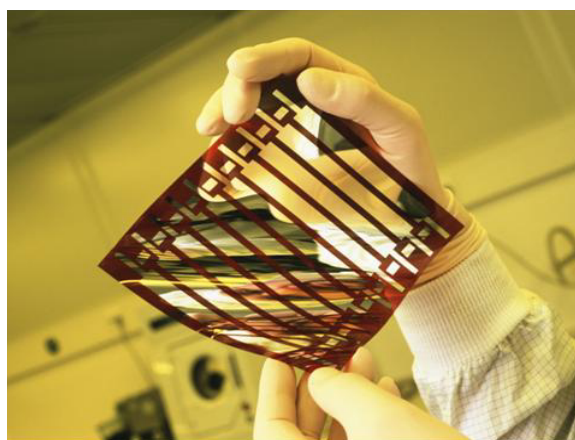


Figure 7 Flexible, plastic PV cell

devices. The molecules and materials from which these devices are made vary considerably, with polymers, organic molecules, inorganic molecules, quantum dots, and other nanostructures all contributing equally to the field. The large array of options provides ample scope for researchers to develop novel solutions for improving device performance.

Despite the promise of photovoltaics based on organics, significant challenges must be overcome to develop molecular structures and cells that operate efficiently and are stable for long-term operation under one-sun solar conditions. Four key areas that need to be explored are outlined below.

Photon Energy Management in Organic and Hybrid Photovoltaic Devices. Current state-of-the-art organic and hybrid PV cells produce a photovoltage that is considerably less than is feasible on the basis of thermodynamic principles. Solving this problem should lead directly to a threefold increase in overall cell efficiency. Although recent investigations have shed some light on the reasons for the low photovoltage, researchers lack a clear understanding of the factors that control this parameter. Basic science investigations are needed to correlate the chemical and physical properties of the active layers with their performance in operating PV devices. Sustained work in this area could have a substantial payoff in improved cell efficiency.

Organic and Hybrid Photovoltaic Layers and Cell Architectures. Organic-inorganic hybrid layers will provide opportunities for the use of different building blocks in the fabrication of PV cells, allowing researchers to combine the best properties of organic and inorganic structures. The fabrication methods developed could allow the assembly of high-efficiency tandem device structures to extract energy from the different wavelengths of sunlight, thereby leading to a substantial improvement in solar-to-electrical energy conversion. More complex fabrication techniques may also allow the integration of photonic structures to allow wavelength shifting and optical field concentration, which would also lead to substantial increases in cell efficiencies.

The light-absorbing and semiconducting properties of quantum structures (e.g., nanoparticles, nanorods, and more complex structures), combined with the range of properties accessible with organic semiconducting polymers, afford new active layers for PV cells that could enhance efficiency. Fabrication methods, such as novel vapor deposition techniques, and solution processing methods, such as layer-by-layer deposition, could allow construction of layers and structures with precise control over the three-dimensional architecture of the active components.

Chemical Discovery and Synthesis. Improved molecular, polymer, and nanocrystal building blocks are needed to address such issues as (1) light harvesting across the visible and near-infrared spectrum, (2) electron donor and acceptor properties, (3) electronic (semiconducting) properties, (4) charge transport in the solid state, and (5) nonlinear optical properties. While many materials are already available, systematic chemical discovery and synthesis are needed to broaden the scope of materials and to allow the development of improved synthetic methods to lower costs and improve purity.

Properties of Organic and Hybrid Photovoltaic Structures. Many basic science questions need to be addressed to better understand the fundamental steps involved in energy conversion in organic and hybrid systems. First, the morphology of the solid-state PV film needs to be defined, then researchers need to develop an understanding of the relationship between the morphology and the structure of the building blocks, the nature of the substrate, and the deposition method used to fabricate the film. Physical methods are needed to elucidate the thermodynamics and dynamics of the fundamental steps of light absorption and exciton generation, charge carrier generation, and charge carrier diffusion to the collector electrodes. To obtain cells that are durable enough for long-term use, photostability and photochemical degradation pathways need to be improved.

Achieving the long-term objective of an organic PV solar cell with a power conversion efficiency that approaches 50% will require solar cells that can extract more of the photon energy available within the solar spectrum. This can be achieved through one of two methods:

- (1) A device architecture designed to match individual solar photons, such as the tandem solar cell (see Figure 8);
- (2) Up-conversion or down-conversion of the solar photons to match an existing single-junction PV design (see Figure 9).

While the first method requires specific design characteristics of the PV structures to have absorption profiles that match the solar spectrum, combined with balanced charge-carrier transport properties, the second requires control of the material to efficiently shift the photon frequencies.

An intrinsic feature of the organic solar cell is the diversity of interfaces; either between dissimilar organic materials acting as the photoconversion layer; with the contact electrodes, where transparency and good ohmic contact are essential; or between multiple layers in a tandem design, where carrier annihilation must be facilitated. These features provide additional challenges that can be met through molecular design and an understanding of electronic interactions at an interface.

Photoelectrochemistry

Photoelectrochemical (PEC) systems provide the best-known wet chemical method of converting sunlight into electrical energy or chemical fuels. PEC systems developed during the mid-1970s and 1980s for capture and conversion of solar energy into electricity and fuels are based on a semiconductor electrode in contact with an electrolyte solution (Memming 2001; Bard et al. 2002; Nozik and Memming 1996; Nozik 1978; Grätzel 2001). The solid-liquid configuration offers the following four advantages: (1) the junction required for efficient charge separation of photogenerated electrons and holes is very easily formed by simply immersing the semiconductor in an appropriate electrolyte solution; (2) the liquid electrolyte offers the capability of a readily conformable and strain-free junction; (3) a third electrode can be added to PEC cells to provide in-situ chemical storage for 24-hr/day power; and (4) the conversion of

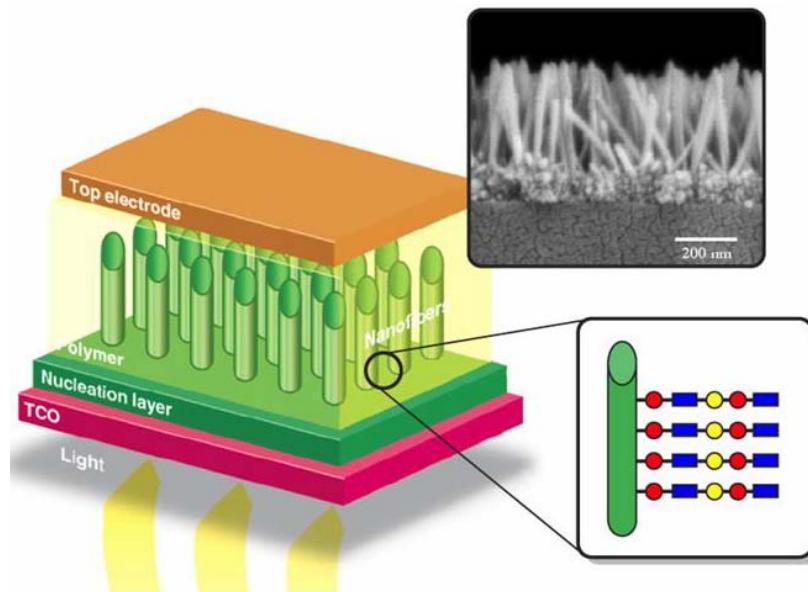


Figure 8 Structure for high-efficiency (50%) organic PV cell based on a nanostructured substrate onto which thin layers of molecular multi-junctions are grown and anchored onto the nanostructure surface. The red circle denotes an electron acceptor; the blue square, an electron donor; and the yellow circle, a metal nanoparticle.

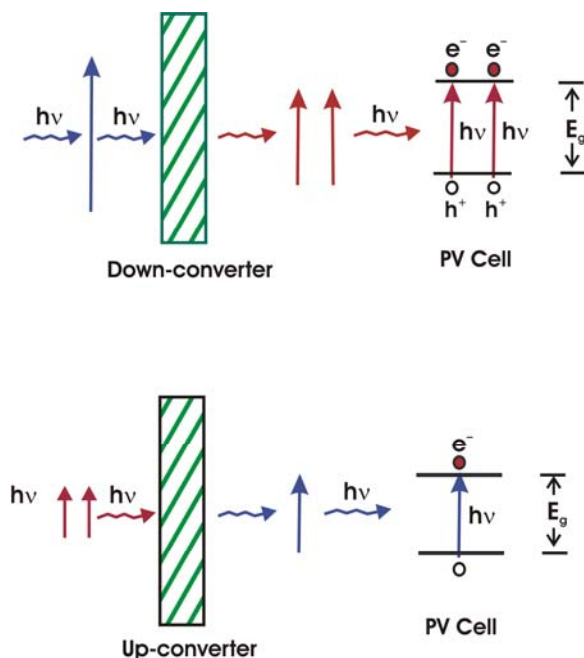
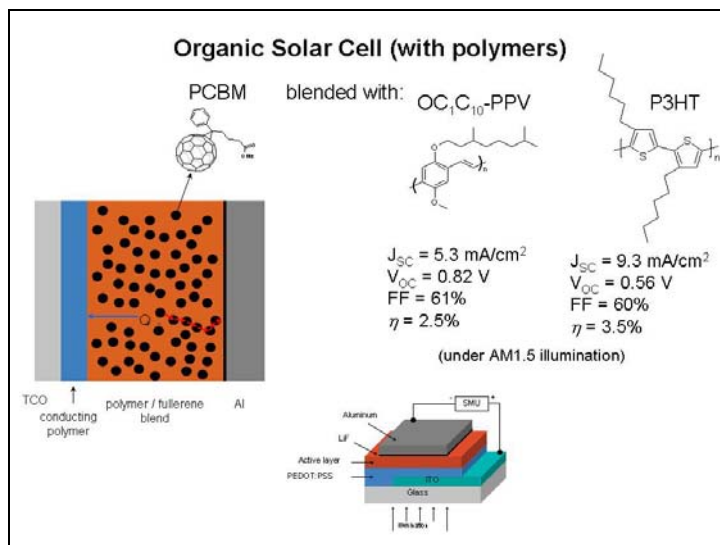
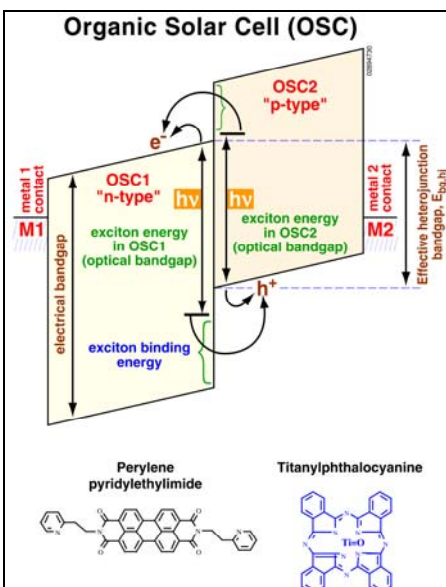


Figure 9 Down-conversion of incident solar photons splits the energy of high-energy photons into two photons of lower energy that can then be absorbed in the PV device more closely matched to the band gap energy and thus avoid thermalization (i.e., heating) losses. Up-conversion adds the energies of two lower-energy incident photons that otherwise would pass through the PV device to produce a single, higher-energy photon that is equal to or greater than the band gap and can therefore be absorbed.

ORGANIC PV CELLS

Organic solar cells also operate with junctions, but the n-type and p-type semiconductors are organic compounds, and the interfacial junction between the n- and p-type regions does not produce an electric field and serves a different purpose than the inorganic p-n junctions. Furthermore, when electrons and holes are produced upon light absorption in organic solar cells, the negative electrons and positive holes become bound to one another through strong attractive electrical forces and form coupled electron-hole pairs, which have been labeled excitons. These excitons have no net electrical charge and cannot carry current — they must be broken apart, or dissociated, in order to produce the free electrons and holes required in the cell to produce electrical power. This is the function of the junction between the n- and p-type organic compounds — when the excitons diffuse to this region of the cell, they split apart and produce the required free electrons and holes. Also, organic solar cells have electrical contacts with different electronic properties.

The organic components of the n- and p-type regions of the organic solar cells can be either molecular semiconductors (like an n-type perylene and a p-type phthalocyanine) or semiconducting polymers (like a p-type polyphenylvinylidene or polythiophene and an n-type fullerene). The figures show the PV cell with both types of organic components and their corresponding chemical structures.



light energy directly into fuel eliminates the need for external wires and a separate electrolyzer. The PEC approach to solar energy conversion has achieved high efficiencies for both electrical power (>15%) and hydrogen generation (>10%). However, photoelectrode lifetime and cost issues have restricted commercialization efforts to date (Memming 2001; Bard et al. 2002; Nozik and Memming 1996).

The electric field formed by the junction at the semiconductor-electrolyte interface plays a large role in efficiently separating the electron-hole pairs created by light absorption. When electrons or holes cross the interface between the semiconductor and the electrolyte, they can drive chemical oxidation or reduction half-reactions at the semiconductor surface to produce either fuels (e.g., hydrogen, reduced carbon, ammonia) or, in a regenerative photovoltaic configuration, DC electrical power. In the latter case, termed an electrochemical photovoltaic (EPV) cell, the oxidation and reduction half-reactions at the two cell electrodes are the inverse of one another, thus producing no net change in the electrolyte. In the former case, the oxidation and reduction half-reactions at the two electrodes are different, and their sum produces a net chemical change in the electrolyte (e.g., decomposition of water into H_2 and O_2).

One critical property of the photoactive material in either a PV or a PEC system is the minority carrier diffusion length (i.e., the distance that electrons or holes created upon light absorption can travel in the structure before they recombine to produce heat). If the minority carrier diffusion length is too short, photogenerated carriers cannot reach the interface to drive the desired reactions and produce output power in the form of electricity or fuels. This is the basic limitation of cheap absorbers: because they have a large concentration of impurities and defects, and therefore have a short minority carrier diffusion length, they generally produce PV cells with low efficiencies. However, the development of nanoscale materials has rescaled the diffusion length requirements, because the minority carrier diffusion length need only be comparable to the dimensions of the sub-units of the nanostructured device (typically a few tens of nanometers). The liquid contact in PEC systems is ideally suited for nanostructured devices, guaranteeing complete filling of the gaps within the porous structures. The goal is to improve the efficiency of such systems by a factor of 2–3, while ensuring stability and robust performance for periods of years in sunlight under maximum load conditions.

Another key advantage of PEC cells is that they naturally offer the opportunity to integrate the energy conversion and storage functions. Photoelectrochemical cells have been shown to directly split water into H_2 and O_2 , thereby providing a basis for the renewable, clean production of hydrogen from sunlight. The materials can be cheap polycrystalline forms, because of the relaxed requirements on the minority carrier diffusion length. However, the known materials, which are robust in water splitting, are not responsive to a wide portion of the solar radiation spectrum; they work best in the ultraviolet (UV) — yielding relatively low efficiencies at the surface of the Earth. Finding new photoelectrodes, either individually or in combination, that can allow the efficient, integrated conversion of sunlight to chemical fuels is one of the primary aims of solar energy conversion research. The goal is to identify PEC systems that display the same efficiency and stability for visible-light-induced water splitting as those demonstrated for near-UV-light-induced water splitting. Closing this gap will lead to the development of cheap and efficient systems that, in an integrated fashion, could produce chemical fuels (e.g., hydrogen) directly from sunlight and therefore directly address, not only the conversion, but also the storage issues, associated with solar energy conversion schemes.

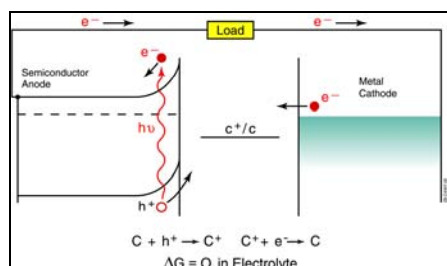
These examples illustrate the central role played by nanostructured systems in the renaissance of PEC systems, which are poised to make an important contribution to solar energy conversion and storage. Additional basic scientific research will support the development of improvements in the existing nanostructured cell and photoelectrolysis approaches and will also support the discovery of disruptive technologies that can dramatically accelerate progress toward high-efficiency solar photon conversion technologies at low cost.

PHOTOELECTROCHEMICAL SOLAR CELLS

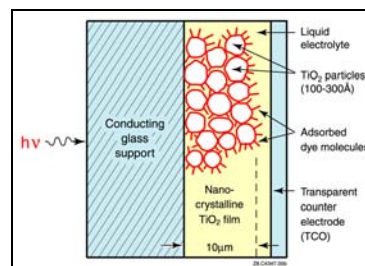
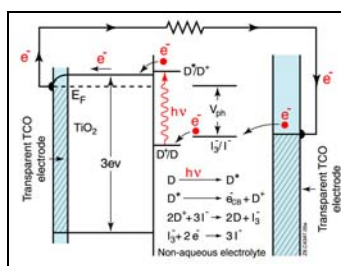
Photoelectrochemical (PEC) solar cells are based on hybrid structures of inorganic semiconductors and molecular structures. In one configuration (called an electrochemical photovoltaic [EPV] cell), a semiconductor is in contact with an electrically conducting liquid (called an electrolyte) that also contains a chemical species (called a reduction-oxidation or redox couple) that can readily donate electrons to and accept electrons from an electrode. The semiconductor forms a junction with the liquid by simple immersion and develops an electric field at its surface. The semiconductor can be n-type or p-type. Upon illumination of the semiconductor, the photogenerated electrons and holes can separate because of the surface electric field. For n-type semiconductors, the holes move to the surface and are captured by the redox couple; the electrons move to the back side of the semiconductor, where they leave the cell via an electrical contact, deliver electrical power to an external load, and then return to the cell at the second electrode. Here, they are captured by the redox species that initially captured the hole at the semiconductor surface; this process returns the redox species to its original condition. Thus the redox couple accepts holes at one electrode and accepts electrons at the other electrode — resulting in charge neutralization and no net change in the redox species. The electrolyte and redox couple just serves to complete the electrical circuit and to produce the electric field required for charge separation.

In a second configuration, dye molecules that absorb sunlight are adsorbed onto thin films of sintered nanocrystalline particles of TiO_2 . The TiO_2 does not absorb much of the sunlight because its band gap is too big (3.0 eV); rather, the dye molecules absorb the sunlight and produce an energetic state (called an excited state). The excited state of the dye molecules results in the injection of electrons into the TiO_2 , creating a positively charged dye molecule (the hole); this phenomenon produces the charge separation required for a PV cell. The TiO_2 film is in contact with an electrolyte containing a redox couple. The circuit is completed when the electrons return to the cell, are captured by a redox species at the second electrode (usually a metal), which then diffuses to the TiO_2 film, where it donates electrons to the positively charged dye sitting on the TiO_2 surface to neutralize it, returning the dye molecules to their original state. Organic solar cells also operate with junctions, but the n-type and p-type semiconductors are organic compounds, and the interfacial junction between the n- and p-type regions does not produce an electric field and serves a different purpose than the inorganic p-n junctions. Furthermore, when electrons and holes are produced upon light absorption in organic solar cells, the negative electrons and positive holes become bound to one another through strong attractive electrical forces and form coupled electron-hole pairs, which have been labeled excitons. These excitons have no net electrical charge and cannot carry current — they must be broken apart, or dissociated, in order to produce the free electrons and holes required in the cell to produce electrical power. This is the function of the junction between the n- and p-type organic compounds — when the excitons diffuse to this region of the cell, they split apart and produce the required free electrons and holes. Also, organic solar cells have electrical contacts with different electronic properties.

Electrochemical Solar Cell

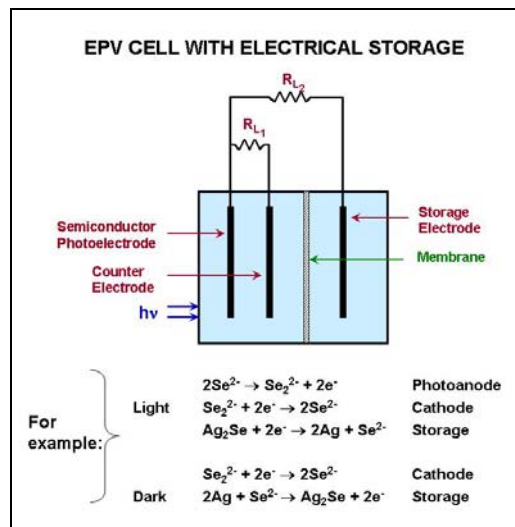
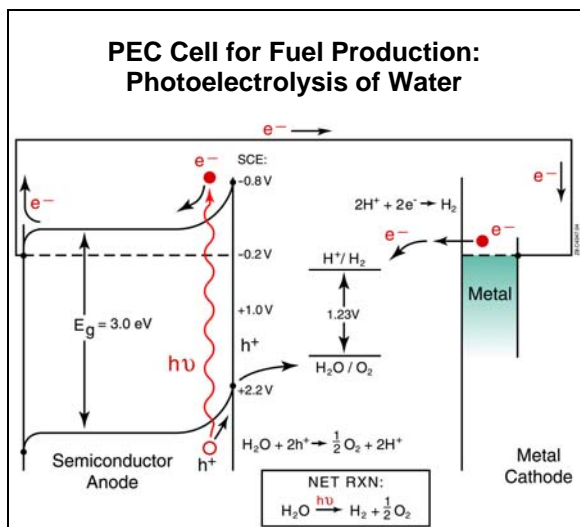


Dye-sensitized Nanocrystalline Solar Cell



PHOTOELECTROCHEMICAL STORAGE CELLS

In addition to photoelectrochemical cells that produce solar electricity as PV devices, PEC cells can also store solar energy as solar-generated fuel (for example, hydrogen in a photoelectrolysis cell), or they can store electricity in a third-electrode PV cell. In a photoelectrolysis cell (left figure), the semiconductor electrode is in contact with water and, when illuminated, it produces electron-hole pairs that separate. In n-type semiconductor electrodes, the holes move to the surface and oxidize water to oxygen; the electrons flow to a second metal electrode, where they reduce water to hydrogen. In p-type semiconductor electrodes, the roles of the two electrodes are reversed, and hydrogen is produced at the semiconductor electrode. In an electrical storage cell, some of the photocurrent generated during illumination is sent to the third storage electrode to charge it. Then, during periods of no illumination, the third electrode discharges, thus maintaining constant power output. The electrochemical electrode reactions for this cell are illustrated in the figure on the right.



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BASIC RESEARCH CHALLENGES FOR SOLAR FUELS

Because of the day/night variation of the solar resource, the practical use of solar energy faces two overarching technological challenges: economically converting sunlight into useful energy, and storing and dispatching that converted energy to end users in an economical, convenient form. To provide base load power, solar electricity and any other solar energy conversion system will require a tightly integrated storage and distribution technology to provide energy to end users in accord with demand. Additionally, there must be a means to cost-effectively convert this energy into forms useful for transportation, residential, and industrial applications. Because these sectors currently use chemical fuels as their primary energy feedstock, one of the following three options must occur: (1) solar electricity must be converted into chemical fuels that could be used in the existing distribution and end-use infrastructure; (2) the distribution and end-use infrastructure must be converted to one that allows widespread, direct use of electricity, which also must be stored until use; or (3) solar energy must be directly converted into useful chemical fuels. Put simply, without cost-effective global transmission, storage, and/or fuel formation, solar electricity can only be a (large) niche market serving as a supplement for other primary sources of energy.

Conversion of electricity into chemical fuels, through electrolysis of water to produce H_2 and O_2 , is an existing technology. However, it is a very expensive method of making H_2 (as discussed below), and the catalysts that are used in current electrolyzers cannot readily scale to the levels that would be needed to support a TW-level implementation of solar electricity use in H_2 production. Direct production of fuels from sunlight is advantageous because it inherently provides a method for extracting energy during the night and for dispatching and distributing energy cost effectively in the existing infrastructure for use in the residential, industrial, and transportation sectors. The ability to use sunlight to produce CH_4 or H_2 from abundant, non-toxic resources such as CO_2 and water, respectively, would revolutionize the economical, environmentally sound production of fuels.

Photosynthetic solar energy conversion has produced the vast majority of the energy that fuels human society and sustains life on Earth. This global-scale, time-tested energy conversion and storage process produces all current biomass and, over geologic time, has produced all the fossil fuels available today. The drawback is that, with current plant types, a large-scale implementation of biomass as a primary energy source would require very large areas of land to make a material contribution to meeting current energy demands. Using the best-known plant for energy production, switchgrass, as an example, production of 10 TW of average power would require covering 10% of the land on Earth (i.e., essentially all of the cultivable land on Earth that is not currently used for agriculture) would have to be covered with biomass farms. Such a large deployment would also clearly stress our ability to provide fresh water to grow such crops; would constrain land use on a global scale; and would impose serious infrastructural constraints to effectively and constantly manage, harvest, and optimally exploit all of the crops over such a large land area. Hence, practical constraints dictate that (1) the efficiency of photosynthesis be increased so that less land area (likely by a factor of 5–10) is required and/or (2) that artificial photosynthetic systems be developed that either borrow components from natural systems or are inspired by the natural system's components to produce useful chemical fuels directly from sunlight with higher efficiencies than the natural system and with an acceptably low cost.

The key challenges involved in cost-effective formation of solar fuels are therefore as follows:

- (1) Use advances in biotechnology to genetically engineer plants to more efficiently — by a factor of 10 — harvest solar energy into biomass, so as to require less land area to produce the needed amount of stored biomass energy;
- (2) Genetically engineer photosynthetic bacterial organisms to produce solar-derived fuels;
- (3) Replicate the essential components of the machinery of photosynthesis outside of a natural organism or plant (i.e., in an artificial photosynthetic system) and obtain the needed ten- or hundred-fold efficiency improvement in a robust, cost-effective system;
- (4) Construct entirely man-made chemical components (out of either organic or inorganic molecules or inorganic semiconductor particles) that, as an assembly, mimic photosynthesis by absorbing sunlight and converting the energy into chemical fuels such as CH_4 and H_2 ; the process developed must be efficient, robust, scaleable, and cost-effective.

Each of these endeavors has significant knowledge gaps that need to be bridged to provide the basis for a viable and economically acceptable energy conversion technology. For example, artificial photosynthetic systems constructed from the key components of photosynthesis can effectively separate charge after absorption of light, but they cannot now be assembled robustly with the needed membranes and catalysts to sustain fuel production. Systems that use man-made chemical components can effectively form fuels, but they either require a consumable chemical reagent as input to the system, or they cease to function after a short time period in the laboratory. Systems based on semiconducting particles either become corroded in sunlight or the systems that are stable become inefficient when irradiated with visible light and only work well in ultraviolet (UV) light.

The challenges involve some of the most fundamental questions in chemistry, materials science, and molecular biology: How can we direct and control the non-covalent assembly of a complex system of molecules to achieve a desired structure and function? How can we mimic the role of a protein matrix without reconstructing that entire protein *de novo*? Can we develop effective catalysts that can take separated charges — regardless of whether they are produced from solar electric photovoltaic (PV) cells or from molecule-based, light-absorbing assemblies — and convert those electrical charges into chemical fuels efficiently and without excessive energy losses during the process? These fundamental research efforts, targeted toward effective and robust solar energy conversion systems, form the basis for the priority research directions (PRDs) on solar fuels that are summarized as the outcome of the workshop.

In the first part of this Panel Survey, we discuss current efforts to exploit recent breakthroughs in molecular biology to optimize the production of biomass. Much of this new understanding derives from the development of a detailed picture of how the molecular machinery of photosynthesis captures and converts sunlight into chemical energy. The discovery of structural

information about the proteins that perform primary photosynthetic energy conversion is driving the surge in new information on how this process works.

The second part of this survey discusses current advances in the field of photosynthesis and explains how this knowledge may be exploited to develop bio-inspired systems for solar fuels production.

The use of robust bio-inspired chemical systems to carry out the primary processes that lead to the photoconversion and use of solar energy to produce fuels is detailed in the third section of this survey. Prototype systems have demonstrated the fundamental steps necessary to complete the photoconversion process, yet many challenges remain, including finding ways to integrate subsystems for optimal performance and understanding the fundamental concepts of energy and charge flow within complex integrated systems.

In the fourth section of the survey, we focus on the design of catalysts that can use the chemical energy derived from sunlight to carry out the critical fuel formation step. Because this research area is still in its infancy, many important challenges remain, such as developing ways to use multiple solar-derived charges to catalyze CH_4 and H_2 production. Finally, we discuss some of the major scientific challenges at the cutting edge of knowledge: integrating subsystems for photo-driven solar fuels formation, optimizing their performance, and providing a versatile and dependable means to ensure their long functional lifetime.

CURRENT STATUS

Biomass-derived Fuels

Biomass has been used as an energy source over the entire span of human existence. It has been, and continues to be, a functioning resource for energy production that is being exploited on a significant scale both in developing and industrialized countries. The overall energy efficiency of biomass energy conversion systems is, however, quite low: less than 1% of the incident insolation is stored as chemical fuels. As a consequence, it is important to address new ways to increase the efficiencies of the many biological pathways leading from photosynthetic light capture through the production of polysaccharides and their subsequent conversion into liquid fuels. Improvements may be obtained by genetic modifications of the organisms responsible for the production of biomass and by re-engineering enzyme catalysts that convert biomass into liquid fuels. Current research directions focus largely on secondary energy production from already-available biomass to produce liquid fuels by: (1) increasing cellulose-to-sugar conversion for the production of ethanol; and (2) developing biomass gasification technologies that produce synthesis-gas (syngas) — a mixture of CO and H_2 for use in fuel-forming reactions.

The structures of plants contain large amounts of cellulose that cannot be readily used as a feedstock for producing liquid fuels (Aden et al. 2002). As a consequence, current research has focused on methods for converting cellulose into its component sugars, which can subsequently be converted into ethanol. Methods for treating cellulose to obtain sugars range from acid treatment to using specific enzymes to catalyze this process. By using only the experimentally achieved process parameters and a feedstock cost of \$53/dry ton, the calculated minimum

ethanol selling price is \$2.70/gal. To be cost effective in today's market, the overall cost of ethanol must be reduced by a factor of 3–5. The problem has been found to be more complex than simply finding new methods for cellulose-to-sugar conversion. Plants contain a wide variety of other molecules, whose structural relationships on the nanoscale are unknown. Understanding these relationships could lead to the development of cost-effective methods to break down cellulose and make the sugars available for bioconversion to fuels.

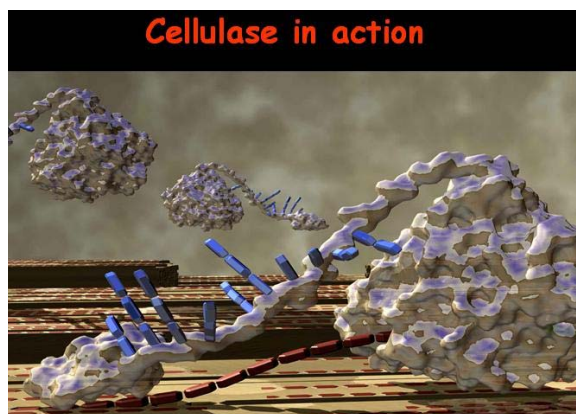
Cellulose is stable both chemically and biologically — a necessary feature in nature, where plants survive the elements for years. Work is underway to understand and develop molecular models of cellulose and the enzymes that hydrolyze it; however, that work has not moved from ideal systems (e.g., ones that do not involve the links to other plant structural components, such as hemicellulose and lignin) to those that are more realistic. The limitations to the rates at which enzymes break down cellulose are not understood either. If researchers could develop an understanding of those limitations, the rates could be increased, allowing shorter residence times and/or reduced enzyme loadings.

The breakdown of cellulose and its related substances leads to mixtures of different sugars. To make a process economically viable, organisms need to convert all of the available sugars to ethanol. Using corn (*Zea mays*) as an example, the ethanol yield could be increased 20% by converting residual starch and the hemicellulose and cellulose in the remaining corn solids into ethanol. Researchers have developed several genetically modified organisms that can ferment multiple sugars; however, the existing organisms are inhibited by other compounds that are naturally present in biomass or are produced in the cellulose-to-sugar conversion process. Understanding how microorganisms respond to inhibitors would assist researchers in developing more robust organisms. Likewise, understanding the metabolic rates within organisms would help researchers develop organisms that convert sugars to fuels more rapidly.

Biomass can be converted into fuels by using direct thermochemical processes (U.S. Department of Energy [DOE] 2003). One of those processes involves gasification of the biomass to syngas and subsequent catalytic conversion of the syngas to produce fuels. Another involves pyrolysis of the biomass to produce oil that can be reformed to liquid fuels. Gasification is well understood, and a commercial-scale facility that gasifies biomass and uses the syngas in a combined-cycle power production process has been in operation for several years. The syngas produced from biomass is similar to that produced by coal gasification, so the process used to

BIOMASS TO FUELS

Improving the yields of fuels from biomass requires substantial effort to understand the detailed processes involved in fully utilizing existing resources. For example, microorganisms that are capable of fermenting sugars to ethanol cannot act directly on cellulose, the major structural component of plants, which accounts for a significant fraction of the total biomass. Research into enhancing the performance of enzymes, such as cellulase, that break down cellulose into its component sugar glucose would significantly enhance the use of the total plant biomass to produce ethanol for fuel. A molecular model illustrating the action of the enzyme cellulase on a cellulose molecule is shown schematically below.



convert it into H₂ and liquid fuels has also been achieved on a commercial scale. One of the issues preventing these processes from being economically viable is the rapid poisoning of the catalysts used in these processes.

The pyrolysis of biomass leading to the production of oil is not as well understood as gasification. To make this oil suitable for commercial use, researchers need to overcome the instability of the oil caused by chemically reactive impurities, phase separation, and acidity. Standards relating to minimal stability requirements for the oil have not been developed, so the required stability and how to achieve it are unknown at this time.

Natural Photosynthetic Systems

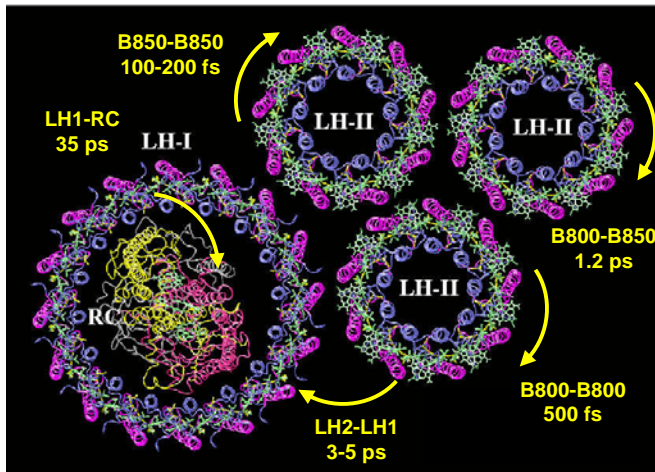
Elucidation of the molecular basis for photosynthesis is essential to optimizing the natural process for biological solar fuels production. It is also essential that researchers provide both proof of concept and inspiration for the construction of artificial photosynthetic devices to produce solar fuels with higher efficiency and more convenience than is offered by existing biomass approaches. Research on natural photosynthetic systems is an active area of study; the goals are to define and understand the structure, composition, and physical principles of photosynthetic energy conversion. In photosynthetic organisms, light is harvested by antenna systems consisting of pigment-protein complexes that are tuned to the quality of light available (Blankenship 2002). The captured excitation energy is transferred to reaction center (RC) proteins, where it is converted by photoinduced electron transfer into electrochemical potential energy. The resulting oxidizing and reducing equivalents are transported to catalytic sites, where they are used to oxidize water and produce reduced fuels, such as carbohydrates.

Bacterial Photosynthesis. Purple bacteria are among the oldest photosynthetic organisms on Earth and contain the most studied photosynthetic apparatus, which consists of two light-harvesting pigment-protein complexes (LH1 and LH2) and a single type of RC. The structures of the purple bacterial light-harvesting and RC proteins have been determined by means of x-ray crystallography and reveal elegant symmetries that are intimately related to their functions. Both LH1 and LH2 contain cyclic arrays of bacteriochlorophyll (BChl) molecules that capture sunlight and circulate the captured energy within these arrays on approximately a 1-ps time scale (1 trillionth of a second) (McDermott et al. 1995; Roszak et al. 2003; Yang et al. 2001). Energy transfer from LH1 to the RC occurs about ten times more slowly. Carotenoids (molecules similar in structure to beta-carotene, the orange pigment in carrots) present in LH1 and LH2 enhance the light-harvesting capability in the blue-green region of the spectrum, while protecting the complex from photo-oxidative damage (Polivka and Sundstrom 2004).

The structure of the bacterial RC has an intriguing two-fold symmetry and organizes the pigments into two parallel electron transfer pathways, termed the A-side and B-side. However, the RC only uses the A-side pigments for electron transfer. Excitation of a special pair of BChl molecules that serve as the primary electron donor initiates charge separation on a picosecond time scale, followed by subsequent thermal electron transfer steps. The rapidity of the initial

HOW DO PHOTOSYNTHETIC ORGANISMS CAPTURE LIGHT AND SEPARATE CHARGE?

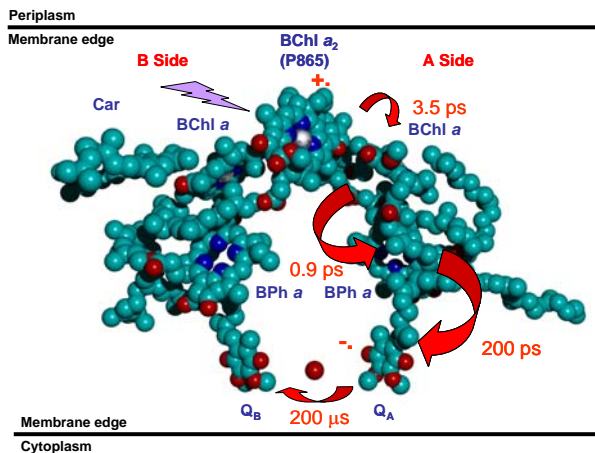
Energy Flow within Bacterial Antenna Proteins and Funneling to the Reaction Center



The image to the left shows the detailed molecular structures of the two light-harvesting proteins, LH1 and LH2, and the reaction center (RC) from a specific species of purple photosynthetic bacteria. The view is looking down onto the plane of the membrane in which these proteins reside. Green plant photosynthesis uses a larger number of proteins, as well as greater numbers of energy and electron transfer cofactors. The bacterial system is illustrative because the issues and questions concerning how energy and electrons flow within and between proteins are similar for all photosynthetic organisms.

The purpose of LH1 and LH2 is to increase the number of solar photons captured and to funnel them into the RC. The closely spaced bacteriochlorophyll molecules shown in green (above) transfer energy within LH1 and LH2 very rapidly, as indicated; this transfer is followed by somewhat slower transfer to the RC. Rapid energy transfer results in efficient utilization of the photon energy.

Photoinduced Charge Separation in a Bacterial Reaction Center

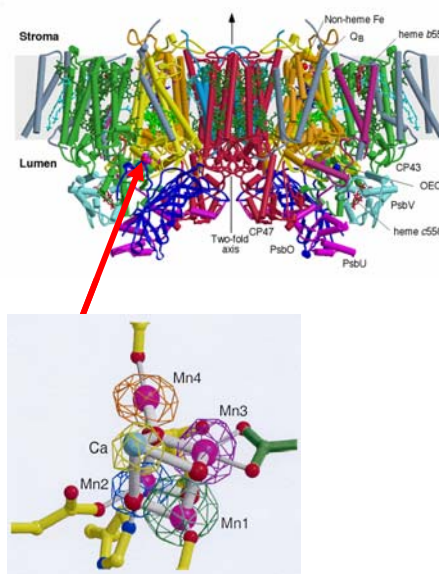
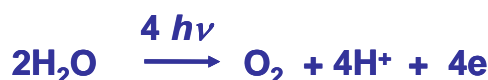


The image to the left shows a side-on view of the RC in the photosynthetic membrane. Only the cofactors responsible for photo-induced charge separation across the membrane are shown. Excitation of the bacteriochlorophyll dimer (BChl a_2) results in rapid electron transfer to an adjacent BChl a acceptor followed by thermal electron transfer to a bacteriopheophytin acceptor (a magnesium-free BChl a that is a better electron acceptor than BChl a). Two more thermal electron transfer events to quinone molecules, Q_A and Q_B , continue to move the electron further from the hole that remains on BChl a_2 . The result is separation of a single electron-hole pair across a 40-Å membrane with nearly 100% quantum efficiency.

The high quantum efficiency of photosynthetic charge separation within the RC results principally from two important features of the structures of the protein and the electron donor-acceptor cofactors. First, the energetics for each electron transfer step are optimized to give the fastest forward rate and the slowest back reaction rate. Second, the electron and hole are moved further away from one another with each electron transfer step, resulting in progressively weaker interactions between them. These factors combine to yield a very long-lived charge separation.

Photosystem I and II in Green Plants and Cyanobacteria.

Photosystem II (PSII) catalyzes one of the most energetically demanding reactions in biology: using the energy of light to drive a catalyst capable of oxidizing water. The crystal structure of PSII, at a resolution of 3.5 Å, reveals that the PSII core complex consists of 19 proteins, while the central protein subunits show striking similarities to the protein structure of the bacterial RC (Ferreira et al. 2004). Photoexcitation of the primary chlorophyll electron donor in the PSII RC once again results in electron transfer, followed by a cascade of thermal electron transfer steps. The important



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difference between the primary donor in PSII and those in PSI and purple bacteria is that the oxidized PSII donor, $P680^+$, is one of the most powerful oxidants known in biology; it provides the oxidizing power to split water into O_2 and H^+ in the Mn-containing, oxygen-evolving complex (OEC) within the protein. Understanding the overall coupling between the photoinduced electron transfer process within PSII and the functioning of the OEC is essential because efficient water splitting, coupled to catalytic reduction of H^+ to H_2 , is one of the most important routes to clean solar fuels (Krauss 2003). The recently determined structure of PSII has provided insights into the organization of the OEC, serves as a framework for describing the water splitting chemistry of PSII, and therefore is of major importance for designing artificial catalytic systems for reproducing this chemistry.

Bio-inspired Approaches to Photochemical Energy Conversion

The construction of artificial photosynthetic systems for practical solar fuels production must incorporate both molecular-level and supra-molecular organization to collect light energy, separate charge, and use charge transport structures to deliver the oxidizing and reducing equivalents to catalytic sites where water oxidation and CO_2 reduction will occur. Thus, a principal target of artificial photosynthetic energy conversion is the environmentally sound production of H_2 directly from water and CH_4 from CO_2 . While some progress has been made on each aspect of this complex problem, researchers have not yet developed components that are both efficient and robust and have not yet integrated the existing functional components into a working system for solar fuels production. The design and development of light-harvesting, photoconversion, and catalytic modules capable of self-ordering and self-assembling into an integrated functional unit will make it possible to realize an efficient artificial photosynthetic system for solar fuels production. It is also imperative to develop systems that will either be defect-tolerant or can execute self-repair strategies to ensure long service lifetimes.

The main focus of current research is the design and synthesis of molecular systems consisting of electron donors and acceptors that mimic the charge separation function of photosynthetic proteins. Researchers have prepared synthetic systems to study the dependencies of electron transfer rate constants on donor-acceptor distance and orientation, the free energy of the reaction, and electronic interaction. The most useful and informative systems are those in which there are structural constraints to control both the distance and the orientation between the electron donors and acceptors. Along with ease of synthesis and stability, bio-inspired systems for photochemical solar energy conversion must have components with intense electronic absorptions that cover the solar spectrum. As is the case in photosynthetic RC proteins, multi-component donor-acceptor arrays that carry out multi-step charge separation reactions are most useful for producing long-lived charge-separated states. Most bio-inspired systems employ light absorbers (i.e., chromophores that absorb broad regions of the solar spectrum) as do the natural chlorophylls. These same chromophores also readily engage in rapid electron transfer reactions leading to stored charges. Unambiguous identification of both the short- and long-lived intermediates produced by photoinitiated electron transfer is critical to determining the mechanisms by which charge separation and storage occur in these bio-inspired systems. This information is generally obtained using time-resolved optical and electron paramagnetic resonance spectroscopy (Levanon et al. 1998).

Efficient Photo-initiated Charge Separation and Storage. The dependence of the rates of electron transfer reactions within covalently linked donor-acceptor molecules on the free energy of the reaction and the electronic interaction between the donor and the acceptor are described well by theory (Marcus 1956). Both theory and experiment show that there is an optimal free energy for achieving the maximum electron transfer rate, and therefore the maximum efficiency, for this process. Moreover, a key prediction of theory is that the rate of an electron transfer reaction will slow when the free energy of the reaction becomes very large. The key to observing this so-called “inverted region” in donor-acceptor molecules is maintaining a fixed distance between the donor and the acceptor as the structure of the donor and/or the acceptor is changed to modify the free energy (Miller et al. 1984; Wasielewski et al. 1985). The use of large free energies for charge recombination to slow these energy-wasting reactions is critical to achieving the long charge separation times essential for driving catalysts for fuel formation.

Another important prediction of electron transfer theory is that the rates (and efficiencies) of electron transfer generally decrease exponentially as a function of distance. Experiments have confirmed this exponential distance dependence and have shown that the steepness of this dependence reflects the molecular structure of the molecules linking the electron donor to the acceptor. Rates of electron transfer reactions generally decrease by about a factor of 30 for every 1 nm of distance (Paddon-Row et al. 1988).

The various electron donors and acceptors used in bio-inspired artificial photosynthetic systems need not be covalently linked to one another. In fact, natural photosynthetic systems use the surrounding protein to position the chlorophyll electron donors and suitable acceptors close to one another. The nature of non-covalent interactions among electron donors and acceptors, such as those found in molecules ranging from DNA to the bacterial photosynthetic RC, is an important area of investigation. Non-covalent assemblies may be constructed through a variety of weak chemical interactions between molecules, e.g., hydrogen bonding, coordination bonding, π - π stacking, formation of donor-acceptor charge transfer complexes, and electrostatic interactions. For example, it has been shown that photogenerated positive charges can move within DNA by means of non-covalent interactions between the stacked base pairs (Lewis et al. 1997).

The importance of using a cascade of thermal electron transfer steps following the initial photoinduced charge separation, as evidenced by natural photosynthesis, has been demonstrated in numerous systems. Studies on the optimization of the free energy changes, distances, and orientations between the various donors and acceptors have allowed researchers to determine strategies for the development of novel molecular structures to tailor the charge separation and storage characteristics to specific applications. For example, efficient performance in the solid state requires (1) the use of specialized donor and/or acceptor molecules, such as C_{60} , that undergo minimal structural changes following electron transfer, or (2) the incorporation of high-potential donors and acceptors to overcome the inability of the solvent to change its structure in the solid state. In these systems, photoinduced charge separation, followed by 1–3 thermal electron transfer steps, leads to overall charge separation efficiencies of about 80% that persist for times approaching seconds (Gust et al. 2001; Wasielewski 1992). Ultrafast laser techniques that measure events down to 20 fs (20 quadrillionths of a second), as well as time-resolved measurements of the magnetic properties of charged intermediates produced within these

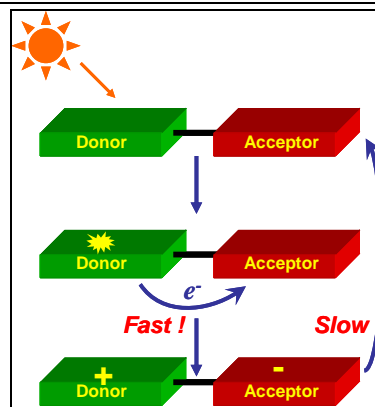
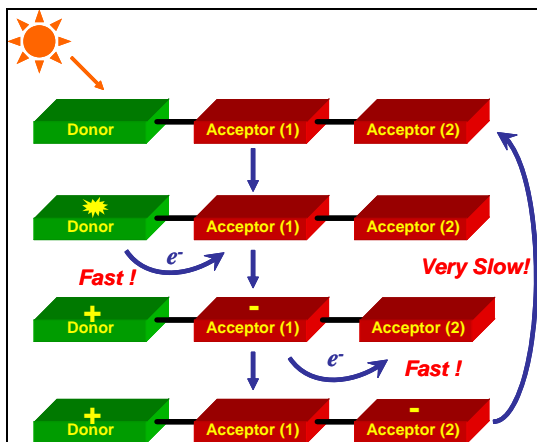
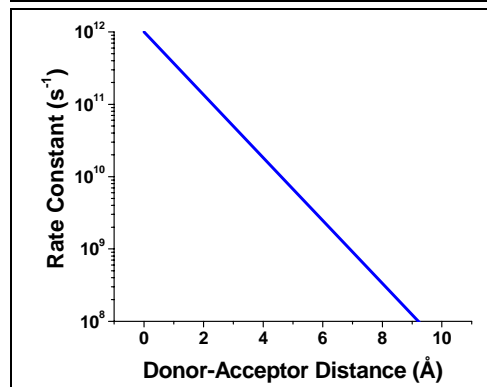
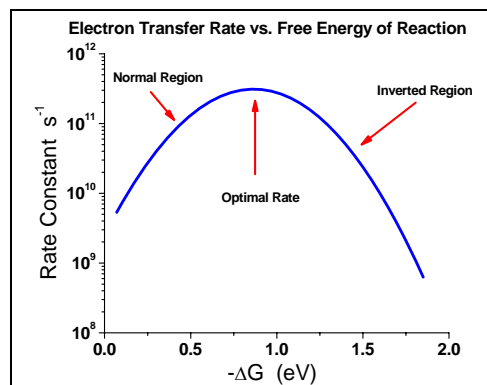
DESIGNING AN ARTIFICIAL REACTION CENTER

Efficient Photoinduced Charge Separation

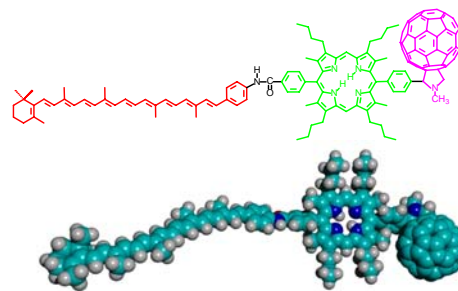
Both theory and experiment show that there is an optimal free energy of reaction for achieving the maximum electron transfer rate (right, top). Moreover, an important prediction of theory is that the rate of an electron transfer reaction slows down when the free energy of reaction becomes very large. The key to observing this so-called "inverted region" in donor-acceptor molecules is maintaining a fixed distance between the donor and the acceptor as the free energy of the reaction is changed. The use of large free energies for charge recombination to slow these energy-wasting reactions is critical to achieving the long charge separation times essential for driving catalysts for fuel formation. As the distance between the donor and the acceptor increases, the electron transfer rate usually decreases exponentially (right, upper middle). The largest ratios of forward-to-back electron transfer rates achieved in a molecule having a single donor and acceptor are about 1,000 to 1 (right, lower middle).

Multi-Step Electron Transfer Provides Long-lived Charge Separation and Storage

Drawing on inspiration from natural photosynthesis, the initial photo-induced electron transfer can be followed by one or more thermal electron (or hole) transfer steps. If each of these steps is optimized with regard to reaction free energy, as indicated above, and the charges move further apart, long-lived charge separation at high quantum efficiencies can be achieved (left, bottom). This has been demonstrated in molecular triads that achieve charge separation quantum efficiencies in excess of 80%, with lifetimes approaching seconds (right, bottom).



Carotene-Porphyrin-Fullerene Triad



artificial RCs, have proven to be important tools to directly gauge the magnitude of the intermolecular interactions responsible for a given rate of electron transfer and determine how this rate depends on the details of molecular structure.

Integrating Artificial Photosynthetic Functions. An antenna, or light-harvesting molecular array, increases the amount of solar energy absorbed without carrying out charge separation itself. Following photoexcitation, a series of one or more energy transfer steps occurs; this series of steps funnels the excitation energy to a site at which charge separation occurs. This process is similar to what occurs in photosynthetic organisms, and it limits the need to produce large amounts of the complex charge separation structures, while maintaining highly efficient light collection. Covalently-linked arrays of light-harvesting chromophores that funnel energy to a central site have been demonstrated, and they require significant synthetic efforts to produce (Seth et al. 1996). By contrast, the ability to create self-assembling, robust, functional antenna arrays is at an early stage of development. For example, new self-assembling antenna systems produced from robust dyes used as industrial paint pigments hold significant promise as antenna molecules (van der Boom et al. 2002). Several systems have been constructed that successfully mimic the light-harvesting, energy-funneling, and charge-separation functions of the photosynthetic RC (Liddell et al. 2004). These include systems in which self-assembly of a light-harvesting antenna structure elicits co-assembly of an appropriate RC to carry out charge separation (Rybitchinski et al. 2004).

Two of the most important photo-driven biological processes are the oxidation of water to O_2 and protons, and proton pumping across membranes. The protons that result from the photo-oxidation of water can be used to produce H_2 . Photo-initiated, multi-step charge separation (using a donor-acceptor triad contained within the walls of a spherical nanoscale compartment made from a lipid, i.e., a liposome) has been used to pump protons to drive the synthesis of ATP, a major energy-rich biological molecule (Figure 10) (Steinberg-Yfrach et al. 1998). In addition, part of the oxidative side of PSII has been modeled by using a multi-step electron transfer cascade to generate a potential sufficiently positive to oxidize a Mn complex (Sun et al. 2001). These examples illustrate the potential of artificial RC components to carry out useful reactions to produce fuels.

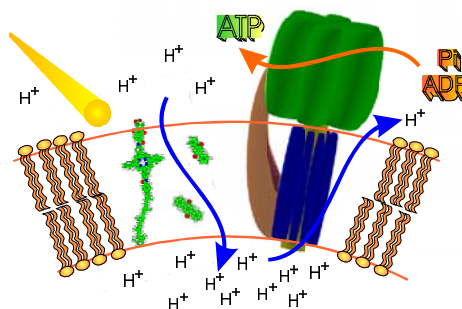


Figure 10 Hybrid light-driven proton pump using charge separation within a donor-acceptor triad and ATP synthase incorporated into a liposome (Source: Steinberg-Yfrach et al. 1998)

Photocatalysis and Photodriven Reactions

Photocatalysis is the process by which absorbed light is used to drive a chemical transformation aided by a catalyst. The catalyst can either absorb the light itself or harness the light absorbed by another molecule. Efficient solar fuel generation requires efficient (1) light absorption, (2) charge separation, and (3) use of the separated charges in fuel-forming reactions (Figure 11). These

reactions must produce the desired fuel (e.g., H_2 , CH_3OH) and a desirable co-product (e.g. O_2 from water oxidation). In so-called heterogeneous (insoluble) catalysts, requirements (1) and (2) are usually implemented by using semiconductor assemblies, while in homogeneous (soluble) catalysts these functions are performed by using molecular assemblies in solution. The critical issue for requirement (3) is the coupling of the one-photon light absorption events in (1) and (2) to the proton-coupled, multi-electron processes required for catalysis. Most previous efforts have used catalysts driven by one-electron reactions to avoid high-energy intermediates. However, fuel production requires multi-electron oxidation and reduction reactions, so new catalysts that couple single-photon events to the accumulation of multiple redox equivalents are essential.

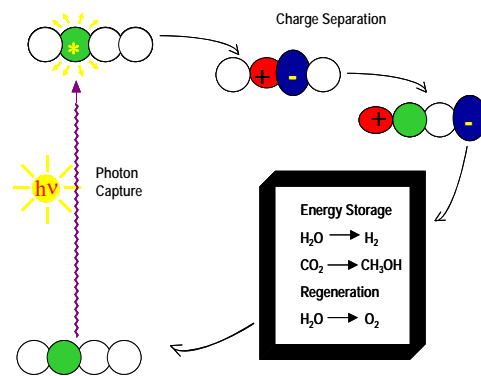


Figure 11 Solar production of fuels by the following sequence: (1) light absorption, (2) charge separation, and (3) use of the separated charges to produce fuel (e.g., H_2 , CH_3OH) and co-product (e.g., O_2 from water oxidation). The reactions shown in the black box require efficient catalysts.

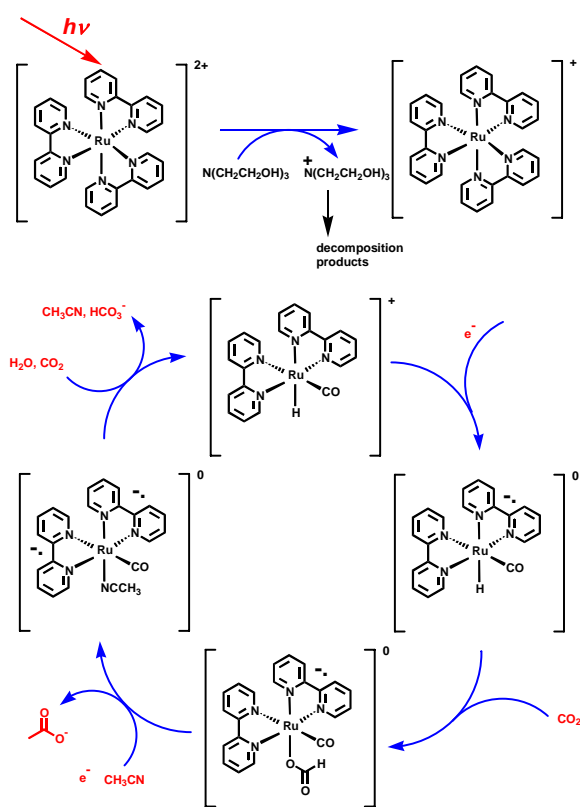
For solar fuel production to be economically and environmentally attractive, the fuels must be formed from abundant, inexpensive raw materials such as water or CO_2 . The thermodynamics for generation of fuels such as H_2 , CH_3OH , or CH_4 by photodecomposition of water or CO_2 from aqueous solutions are known (Arakawa et al. 2001; Sutin et al. 1997). Assuming a 100% charge separation efficiency and a catalyst coverage density of $1/\text{nm}^2$, the catalyst turnover rate must be about 100/s in order for the fuel generation/regeneration reactions to keep up with the solar production of electrons and/or holes. Currently available catalysts for CO_2 reduction or water oxidation have turnover frequencies that are far below those required for a viable catalyst.

Homogeneous Photocatalytic CO_2 Reduction. Most systems studied to date generally use transition metal complexes (e.g., containing Ru and Ir) as catalysts for photoreduction of CO_2 because they absorb a significant part of the solar spectrum, have long-lived excited states (about 1 μs), and can transfer electrons to or from small molecules. Typical systems also include a secondary metal complex (e.g., containing Co) as a co-catalyst to carry out the reduction of CO_2 . Metal hydride complexes are also important because bimolecular reactions of hydrides or their reactions with $\text{H}_2\text{O}/\text{H}_3\text{O}^+$ are responsible for the formation of H_2 . While both metal hydride and metal- CO_2 complexes pertinent to some of the systems are known, in no case has the reduction mechanism been completely determined. For example, the best systems reported thus far show quantum efficiencies as high as 38% using a Re sensitizer, but have disappointing turnover frequencies of CO formation of $<10/\text{h}$.

Homogeneous Photocatalytic Water Oxidation. Photochemical splitting of water into molecular H_2 and O_2 has yet to be realized on a large, cost-effective, efficient scale. Yet recent advances related to this field have been made, including the reported use of a compound containing two interacting Rh atoms to photocatalyze the reduction of HBr to H_2 (Heyduk and

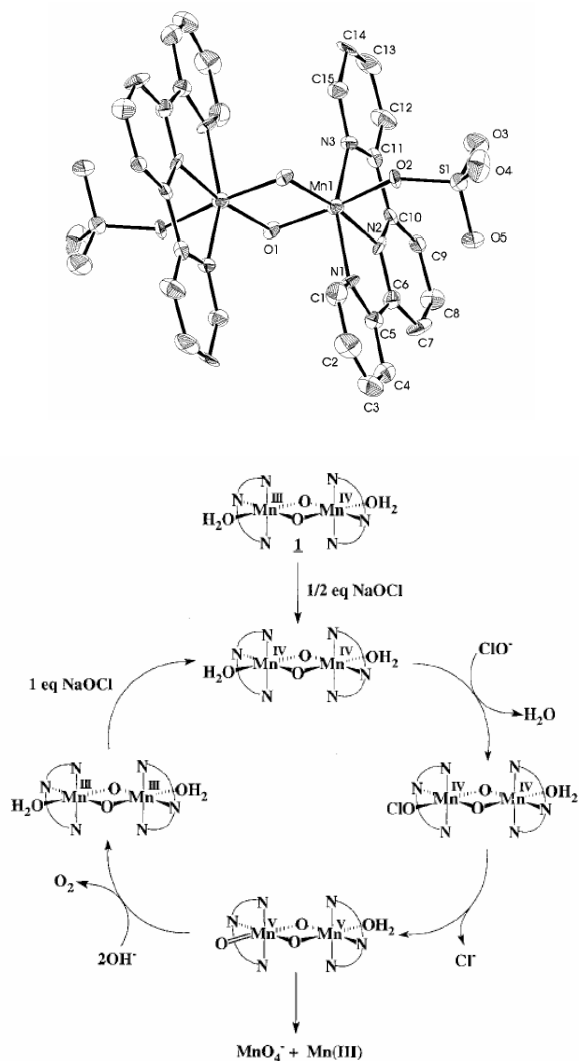
CATALYSTS FOR CO₂ REDUCTION

Photo-driven catalysts for CO₂ reduction have made use of the versatile photochemistry and redox properties of Ru complexes. Photo-excitation of Ru(bpy)₃²⁺ (below, top panel) results in formation of an excited state that reacts readily with the sacrificial donor triethanolamine. The reduced Ru(bpy)₃⁺ can then act as a source of electrons to drive a catalytic cycle of the type shown in the bottom panel below (Pugh et al. 1991). In this cycle, another Ru complex catalyzes the reduction of CO₂ to formate ion. Input of electrons is required at two points in the overall cycle. The overall mechanism for the catalytic reduction of CO₂ is complex, so that a great deal of work remains to find optimal catalysts that are well-coupled to the photochemical agents that use solar energy to provide a source of electrons to drive the catalysts.



CATALYSTS FOR WATER OXIDATION

Catalysts with sufficient oxidizing power to split water remain relatively rare. Yet, several recent catalysts based on Mn and Ru have demonstrated water oxidation following addition of strong oxidants to access the higher oxidation states of these metals. As an example, the top panel shows the structure of a Mn₂ complex that generates O₂ obtained from water using NaOCl as an added oxidant (Limberg et al. 1999). The mechanism of catalysis is shown in the lower panel. Thus far, the turnover frequencies and the stability of water oxidation catalysts remain low. In addition, coupling of a photo-driven oxidant to these catalysts has not been accomplished.



Nocera 2001). All water oxidation catalysts examined to date are based on transition metals that have oxidation states accessible in the 1–1.5 V range. Standing alone among these catalysts is the water oxidation enzyme of PSII in green plants. In its OEC, the enzyme contains a Mn cluster, which is capable of turning over about 10^3 O₂ molecules/s (see *Photosystem II, Using Light to Split Water* sidebar) (Ferreira et al. 2004; Ruettinger and Dismukes 1997). While several transition-metal complexes have been shown to catalyze water oxidation, turnover frequencies remain disappointingly low.

Heterogeneous Semiconductor-based Photocatalysis. In 1972, Fujishima and Honda reported the first complete water photoelectrolysis system (Fujishima and Honda 1972). It was based on an *n*-TiO₂ anode with a small electrical bias to compensate for the insufficient reducing power of electrons in the conduction band of TiO₂ to drive the cathodic water reduction reaction. The requirements for an effective photocatalytic semiconductor are dictated by the positioning of the valence and conduction bands and by chemical stability during the catalytic cycle. In the case of reactions to produce H₂ and O₂, the conduction band must be above 0 V vs. normal hydrogen electrode (NHE) to produce H₂, and the valence band must be below +1.2 V vs. NHE to produce O₂ (Grätzel 1983). Soon after, *n*-SrTiO₃, for which the conduction band is higher in energy than that of TiO₂, was used without an electrical bias (Wrighton et al. 1976). In 1979, photoelectrocatalytic reduction of CO₂ in aqueous suspensions of semiconductor powders was first accomplished (Inoue et al. 1979).

Heterogeneous systems based on photo-driven redox reactions at semiconductor interfaces remain among the most successful approaches to photocatalysis, promising a means of solar energy harvesting and water pollutant degradation. The general strategy involved in these systems relies on the formation of an electron-hole pair upon absorption of a photon by a semiconductor sensitizer (Figure 12). The electron (conduction band) is used to reduce an acceptor in the surrounding medium, while the hole (valence band) is used to oxidize a donor. In addition, catalysts (Pt group metals for reductions and Pt group metal oxides for oxidations) are often added to the semiconductor to facilitate the redox processes after electron-hole formation. Bulk semiconductors offer poor quantum conversion efficiencies (0.1–0.01%) because of low surface areas and significant charge recombination (Grätzel 1983).

The development of high-surface-area semiconductor dispersions and porous thin films has greatly improved the capabilities of semiconductor-based photocatalysts. Semiconductor catalytic dispersions have been made with both solid (e.g., polymers) and liquid (e.g., colloids) supports and can be used to catalyze transformations on both liquid and gaseous substrates.

Semiconductor particle photocatalysis has been the most studied heterogeneous approach to H₂ production (Linsebigler et al. 1995; Kudo et al. 2004). Colloids or nanoparticles offer several advantages over bulk catalysts by having high electron-hole pair separation efficiencies (~100%), large interfacial surface areas, and short electron-hole diffusion lengths to the interface; in addition, they are readily studied by using spectroscopic techniques (Grätzel 1983).

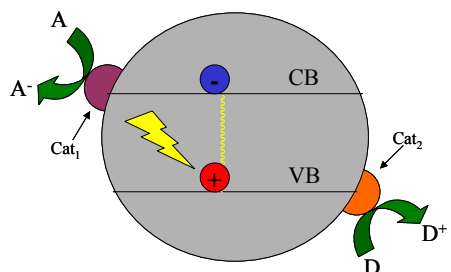


Figure 12 Schematic diagram of photoredox processes at a semiconductor particle

Upon photoexcitation, the electron produced in the semiconductor migrates to the surface and reduces water to H_2 with the aid of Pt metal. La-doped Ta particles loaded with a NiO co-catalyst exhibit the highest efficiency for H_2 and O_2 generation using UV light, with a quantum yield of 56% for sustained periods (>400 h) (Kato et al. 2003). The obvious difficulty in this case is the need for UV light. H_2 and O_2 are produced under visible light at efficiencies in excess of 30% with narrow-band-gap semiconductors but, thus far, a sacrificial reagent is required if a single component is used (Kudo et al. 2004).

Current efforts to improve the efficiency of direct water photolysis focus on band engineering by doping (Tang et al. 2004) or the formation of solid solutions (Kudo et al. 2004). Nitride, oxynitride, and oxysulfide semiconductors, which have band gaps in the visible region of the spectrum, have been studied with sacrificial electron donors and acceptors (Kasahara et al. 2002; Ishikawa et al. 2004). Improved O_2 evolution catalysts are needed to achieve overall water splitting with dye-sensitized semiconductor particles. The most active and stable O_2 evolution catalyst studied to date is colloidal IrO_2 (Morris et al. 2004). Molecular O_2 -evolving catalysts based on Ru and Mn (Limberg et al. 2001) are also interesting as components of microheterogeneous water-splitting systems.

Photoreduction in Porous Materials. Porous materials such as zeolites and molecular sieves, usually made of silica, have been employed as the catalyst support with more success than in the semiconductor systems. In these cases, isolated metal centers such as Ti or Zr are substituted into the silica framework or anchored on the pore surface. When loaded with CO_2 and water and irradiated with UV light, CH_3OH and CH_4 are produced (Matsuoka and Anpo 2003). Recent mechanistic studies indicate that CO_2 splitting to CO is the primary single-photon step, with water acting as the electron source. Reduction of CO_2 to CO is accomplished with longer-wavelength light by charge transfer to Zr from a second metal center (Lin and Frei 2005). This heterogeneous approach is amenable to exploration of other metals such as Ru and Co, which are known to activate CO_2 from studies in homogeneous media. By exploiting the compartmentalized nature of nanoporous supports and developing methods for the precise arrangement of the functionalities, such binuclear sites offer opportunities for exploring CO_2 reduction by water to a carbon-based fuel by means of visible-light, multi-photon schemes (Figure 13) (Hirose et al. 2003).

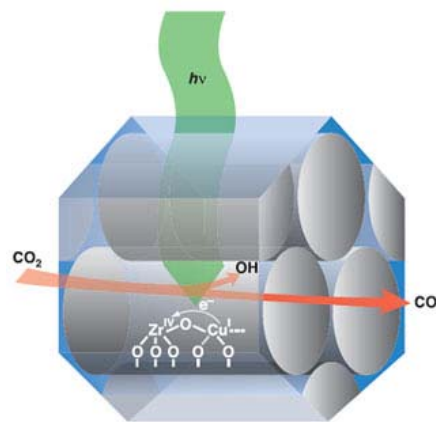


Figure 13 Zr and Cu redox sites on a nanoporous inorganic support carry out the stepwise conversion of CO_2 and water via CO to fuels using visible light in a solvent-free system.

BASIC SCIENCE CHALLENGES, OPPORTUNITIES, AND RESEARCH NEEDS IN SOLAR FUELS PRODUCTION

Biomass-derived Fuels

Photosynthetic light-driven biological processes have enormous capacity for sustainable, carbon-neutral, solar-powered replacement of fossil fuels by fixing more than 100 Gtons of carbon annually, which is roughly equivalent to 100 TW of energy. However, this fixation rate is currently in balance with respiration and other facets of the global carbon cycle, so adding another 10 TW of fixation would require enormous land areas at present. Primary products of photosynthesis include cell wall components such as cellulose and lignin, as well as storage molecules, starch, sugars, lipids, etc. There are also many intermediate metabolites that could lead to a wide range of other potentially useful organic molecules. These in turn, can be bioconverted to a wide range of fuels and value-added chemicals. Through understanding and discovery, it is possible to increase solar-energy-dependent biofuels production by plants and microbes. Challenges associated with achieving this goal include the following: (1) mining biological diversity to discover improved catalysts for biofuels production; (2) capturing the high efficiency of the early steps of photosynthesis to produce high-value chemicals and fuels; (3) understanding and modifying the bioprocesses that constrain biofuels production due to photosynthetic sink limitations, inefficient reductant use, and environmental factors; (4) elucidating plant cell wall structure and understanding how it can be modified and efficiently deconstructed by protein assemblies; (5) extending nitrogen fixation to biofuel crops to reduce dependence on fossil fuel nitrogen fertilizer; and (6) developing an overall deeper understanding of the biological processes needed to improve plants and microbes to increase solar-energy-dependent biofuels production.

Natural Photosynthetic Systems

Natural photosynthesis has achieved the ideal of solar-initiated water splitting coupled to chemical energy storage using abundant, renewable, self-assembling, “soft” matter. The resolution of fundamental structural design principles in natural photosynthesis provides a means to accelerate the discovery of synthetic architectures that embody mechanistic principles used in biology. These principles can be used to realize robust, scalable supramolecular architectures amenable to global energy applications. Two important challenges are (1) the discovery of design principles to maximize the efficiencies of solar energy capture, conversion, and storage; and (2) realization of these enabling principles in advanced biomimetic assemblies where both the supramolecular structures and surrounding supramolecular scaffolds exploit biological designs for function.

Meeting these challenges will require the following: (1) understanding and controlling the weak intermolecular forces governing molecular assembly in natural photosynthesis; (2) understanding the biological machinery for cofactor insertion into proteins and protein subunit assemblies; (3) adapting combinatorial, directed-evolution, and high-throughput screening methods to enhance natural photosynthetic systems to increase the efficiency of solar fuels production; (4) characterizing the structural and mechanistic features of new, natural photosynthetic complexes to identify desirable design motifs for artificial photosynthetic systems; and

(5) determining the physical and chemical rules that underlie the biological mechanisms for repair and photoprotection.

The resolution of structural dynamics across the entire time scale of solar energy conversion is central to the discovery of fundamental design principles for solar energy conversion. Just as ground-state optical absorption spectra cannot reveal the complexity of excited-state reaction dynamics for complex molecular ensembles, static molecular structures cannot reveal the fundamental mechanisms underlying solar energy conversion. Efficient solar energy conversion requires the discovery of mechanisms that control both the ground- and excited-state structural landscapes of complex molecular assemblies — ranging from the attosecond electron dynamics associated with nascent photon absorption and charge separation, to the minutes-and-longer control of atomic motions during the catalytic production of solar fuels. Making these discoveries will require new characterization tools (ultrafast optical, electron paramagnetic resonance, advanced x-ray, neutron scattering, and imaging) to determine structure/function relationships in photosynthetic proteins. Integration of experimental measurements of structural and electronic dynamics with multi-scale theoretical approaches is essential for (1) achieving fundamental breakthroughs in system design paradigms for solar energy capture and conversion by supramolecular structures, and (2) mapping out and predicting optimized ground- and excited-state structural and energy landscapes for efficient solar energy conversion.

Catalytic power and specificity, which are key attributes of enzyme-mediated catalysis, have their origins in the active environment provided by the protein. The same is true in the primary solar energy conversion reactions of photosynthesis. The proteins involved in the light-harvesting complexes and the RCs are not just inert scaffolds. They provide much more than just a means of optimally positioning the chromophores and the electron transfer cofactors. The medium provided by the protein actively promotes, enhances, and indeed controls the light-harvesting and electron-transfer reactions both within the protein and across interfacial protein boundaries. This is a key feature of the natural system that allows it to operate so efficiently. Furthermore, proteins can be readily engineered, via genetic modification, to explore a diversity of structure/function scenarios. Because of major limitations imposed by covalent synthesis of large assemblies, construction of the next generation of bio-inspired solar-energy conversion devices will require placing the chromophores into a “smart matrix” to control their key electronic properties by using weak interactions and self-assembly. Achieving efficient integrated solar energy conversion systems using smart matrices will require the following: (1) learning how natural protein matrices control and optimize energy and charge transport both within a single protein and between proteins; (2) engineering proteins, polymers, membranes, gels, and other ordered molecules to provide tailored active environments (i.e. smart matrices); (3) incorporating bio-inspired cofactors within the designed matrix; (4) integrating multiple cofactor-matrix assemblies to perform the overall function; (5) characterizing the coupling between the cofactors and the matrix in natural and bio-inspired systems by using advanced techniques; and (6) developing smart matrices that compartmentalize incompatible products (e.g., O₂ and H₂).

Bio-inspired Approaches to Photochemical Energy Conversion

A major scientific challenge is the preparation of bio-inspired, molecular assemblies that integrate light absorption, photoinduced charge separation, and catalytic water oxidation/fuel formation into a single unit. These integrated assemblies must take full advantage of both molecular and supramolecular organization to collect light energy and transfer the resulting excitation to artificial RCs. These centers must separate charge and inject electrons and holes into charge transport structures that deliver the oxidizing and reducing equivalents to catalytic sites where water oxidation and CO₂ reduction occur. It is critical to understand how excitation energy flow from the antenna to a RC depends on molecular structure. In addition, charge transport structures for delivery of redox equivalents to catalysts must be developed. By analogy to natural photosynthesis, it is important to provide control elements, or “throttles,” to optimize energy and charge flow within an artificial photosynthetic system as it responds to varying light intensities and spectral distributions. One of the most difficult tasks critical to achieving system integration is coupling single-photon events to the accumulation of multiple-redox equivalents necessary to drive multi-electron, fuel-forming chemistry within a catalyst.

The assembly of complex photoconversion systems with synergistic functionality depends on a variety of weak, intermolecular interactions, rather than strong, individual covalent chemical bonds. A critical step toward fully functional photoconversion systems is the ability to create increasingly larger arrays of interactive molecules. Covalent synthesis of near-macromolecular arrays becomes highly inefficient and costly, thus requiring that practical photoconversion systems be prepared using self-assembly to achieve ordered architectures from properly functionalized building blocks. Self-assembly is based on a variety of weak interactions — such as hydrogen bonding, electrostatic, metal-ligand, and π - π interactions — that give rise to ordered structures. Achieving the goal of producing a functional, integrated artificial photosynthetic system for efficient solar fuels production requires the following: (1) developing innovative architectures for coupling light-harvesting, photoredox, and catalytic components; (2) understanding the relationships between electronic communication and the molecular interactions responsible for self-assembly; (3) understanding and controlling the reactivity of hybrid molecular assemblies on many length scales; and (4) applying new synthetic discoveries in nanoscale materials (e.g., shape and pore control, nano- and microphase separation) to organize functional parts of an integrated artificial photosynthetic system for efficient fuel formation.

Biological systems, such as photosynthesis, have built-in repair mechanisms that can restore useful function following damage to the system. This contrasts strongly with the lack of such mechanisms the complex molecules used to develop artificial photosynthetic systems for solar fuels production. The development of active repair and photoprotection strategies for artificial photosynthetic systems is a major scientific challenge that is critical to the long-term efficient performance of these systems. The usual strategy used by photosynthetic organisms to repair photochemical damage is to degrade the pigment-protein complex and replace it with a newly synthesized complex. Photosynthetic systems are continuously subjected to photochemical damage, especially when the incident light intensity is high. The major scientific challenge lies in understanding the photoprotection and repair mechanisms in natural systems and exploiting these findings to engineer robust artificial systems. To ensure that complex, artificial, photosynthetic systems designed for solar fuels production maintain their efficiency over long lifetimes, the

following challenges must be met: (1) understanding repair and photoprotection mechanisms in natural photosynthesis; (2) exploring assembly-disassembly strategies as a mode of self-repair in artificial photosynthetic systems; (3) developing active repair molecules that specifically identify and target defects in artificial photosynthetic systems and repairing them; and (4) exploring redundancy and distributed function as a strategy to circumvent damage.

Photocatalysis and Photodriven Reactions

Significant scientific challenges remain in the effort to design and synthesize efficient, high-turnover catalysts for the conversion of solar energy into energy-rich fuels. Important reactions include the splitting of water to O_2 and H_2 and the reduction of CO_2 to CH_4 . To carry out these reactions, researchers will need to design and synthesize robust ligands, multi-metallic catalysts, and tailored environments surrounding the catalysts. Guideposts for the development of new systems will come, in part, from the new understanding acquired from bioenergetic enzymes involved in fuel-producing reactions, especially the water-splitting reaction of PSII and the H_2 -producing reaction of hydrogenases. A combination of techniques (ranging from x-ray crystallography and magnetic resonance spectroscopies to genetic engineering) is needed to elucidate the structure and dynamics of the intermediates of catalytic reactions occurring at redox centers of key enzymes involved in solar energy conversion. This knowledge will provide the blueprint necessary to formulate the precise molecular mechanisms of these biological processes and apply them to catalyst design and synthesis.

Newly designed catalysts for fuel formation must rely on complex mechanisms that incorporate multi-electron, atom, and proton-coupled electron-transfer reactions. The need to understand bond-breaking and bond-making processes that accompany electron transfer during fuel-forming transformations will require new synergistic theoretical treatments and mechanistic studies that address these events. Mechanistic studies are therefore essential to the rational design of advanced catalytic systems. Important targets include multi-metallic systems, with particular emphasis on catalysts that use non-noble metals to replace costly and rare noble metals. It is also critical to develop efficient catalysts for solar-driven production of fuels (H_2 , CH_3OH , etc.) that do not depend on consumption of a “sacrificial” molecule. For example, solar-driven water splitting will produce H_2 and O_2 , both of which are consumed to regenerate H_2O when the fuel is used.

With guidance from theoretical calculations, researchers must develop an understanding of catalytic mechanisms at a molecular level, whether the catalyst acts in solution, at interfaces, or on surfaces. In addition, they must understand how catalysts interact with their surrounding environment. This understanding should include detection of the intermediates and identification of their sequence of formation, kinetics, and energetics. The development of molecular strategies to compartmentalize mutually incompatible products, such as H_2 and O_2 , in the fuel formation process is also important. New fuel-forming catalysts must also be integrated into the higher-order assemblies required to construct practical photoelectrochemical devices. To achieve this level of mechanistic understanding, a combination of structural and time-resolved techniques must be employed, together with careful design of model systems that facilitate the application of these techniques.

CONCLUSION

The efficient production of clean solar fuels presents many scientific challenges. Yet progress in this field to date provides a strong argument that this goal is achievable. The major scientific challenges that will need to be addressed are (1) understanding biological mechanisms for the efficient production of fuels from biomass; (2) developing a detailed knowledge of how the molecular machinery of photosynthesis captures and converts sunlight into chemical energy; (3) discovering how to use this knowledge to develop robust, bio-inspired chemical systems to carry out photoconversion; (4) developing catalysts that use photo-generated chemical energy to efficiently produce such fuels as CH₄ and H₂; and (5) developing an integrated photo-driven system for solar fuels formation with optimized performance and a long functional lifetime.

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BASIC RESEARCH CHALLENGES FOR SOLAR THERMAL UTILIZATION

CURRENT STATUS

Solar thermal utilization can be categorized into low-temperature solar thermal systems, which may not involve sunlight concentration, and high-temperature solar thermal systems, which require sunlight concentration. Concentrated photovoltaics (CPVs), although not a solar thermal process, crosscuts with solar thermal utilization through the use of concentrators.

High-temperature Solar Thermal Systems

High-temperature solar systems use various mirror configurations to concentrate the light and then convert the sun's energy into high-temperature heat. The heat can be converted into electricity through a generator, or it can be used to drive chemical reactions. A plant consists of three parts: an optical system that collects and concentrates the light, a receiver or reactor that converts the light to heat, and an “engine” that converts heat to electricity or “reactor” that converts heat to chemical potential.

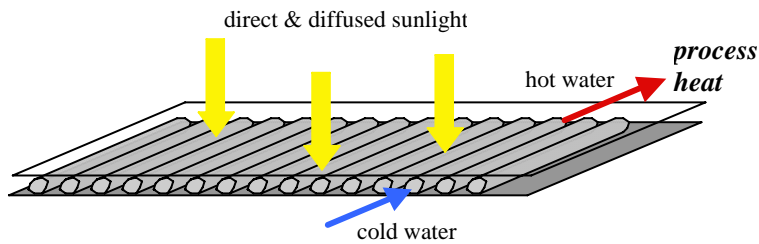
We will survey the principles and state of the art of the optical systems used for concentration, discuss the engines or other components that convert the concentrated heat into electricity, and finally evaluate the state of the art for reactors that convert the heat into chemical fuels.

Solar Concentrators

The current status of solar concentrators, including current research directions, is treated in the Solar Thermal Technology Assessment, Appendix 1. We offer a brief survey for the convenience of the reader.

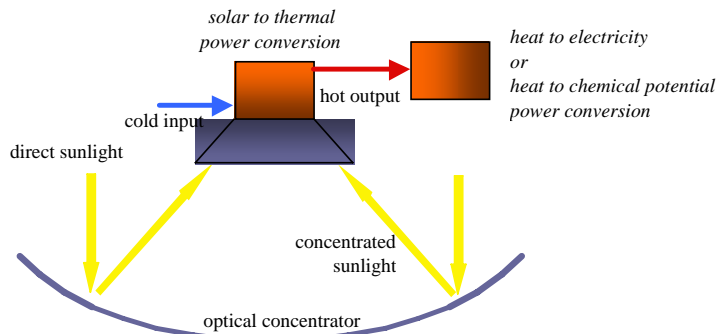
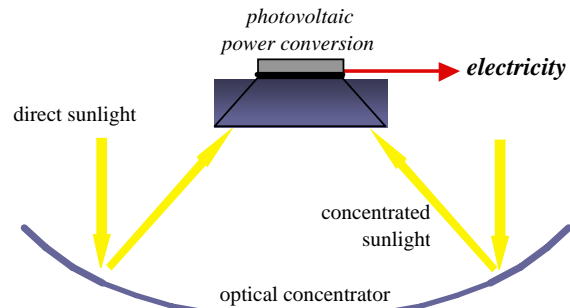
Line Focus Systems. In line focus systems, incident sunlight is “folded” from a plane to a line. In most cases, the optical configuration is that of a trough tracking the sun from east to west and a target that rotates accordingly (Figure 14a). The main inherent advantage of the system is its compatibility with large engines (i.e., steam turbines of hundreds of megawatts). The main inherent disadvantage is the low operating temperature, limited to less than 750K by the relatively low concentration and long tubular receiver configuration. Lower temperatures reduce the efficiency of the heat transfer to the fluid located in the tubular receiver; this fluid provides the thermal energy to drive electricity generation cycles. The current systems range from 350 MWe to newer small-scale 1-MWe systems. Current installed cost is approximately \$3/W; the short-term goal is to reduce this cost to \$2/W.

THREE TYPES OF CONCENTRATED SOLAR "THERMAL" SYSTEMS



Low-temperature solar thermal systems. This system does not involve sunlight concentration, or occasionally may employ low-concentration ($C \leq 2$). This system is suitable for home use where it usually heats hot water for direct use or home heating.

Concentrated photovoltaic (CPV) system. Concentrated photovoltaics, although not a solar thermal process, is included in this survey because of the utilization of concentrators.



High-temperature solar thermal systems. Such systems require optical concentration of direct sunlight at a ratio varying from about 20 to several thousands, depending on the specific process and system involved. Concentrated solar thermal systems are large megawatt(electric) systems that can be used for electricity generation or fuel production.

Central Receiver Systems. Central receiver systems contain an array of Fresnel reflectors (heliostats) with two axes of rotation. The common focus is stationary, located on a solar tower (Figure 14b). The two-axis tracking enables a higher concentration ratio and the higher operating temperatures and power conversion efficiency than those of the line focus configuration. However, as the system size increases, the optical efficiency (the ratio of sunlight capture to incident sunlight) declines. Thus, system optimization is required.

Two 10-MWe facilities are situated in the United States near Barstow, California, and one 2.5-MWe facility is in Almaria, Spain. Present estimates of large-scale (>50-MW) facility costs are about \$3/W (Sargent & Lundy 2003; Stoddard et al. 2005). A recent study (Pitz-Paal et al. 2005) indicates that the new developments discussed here should lead to a cost reduction of at least \$0.5/W. Materials development aimed at high-temperature performance would impact efficiency.

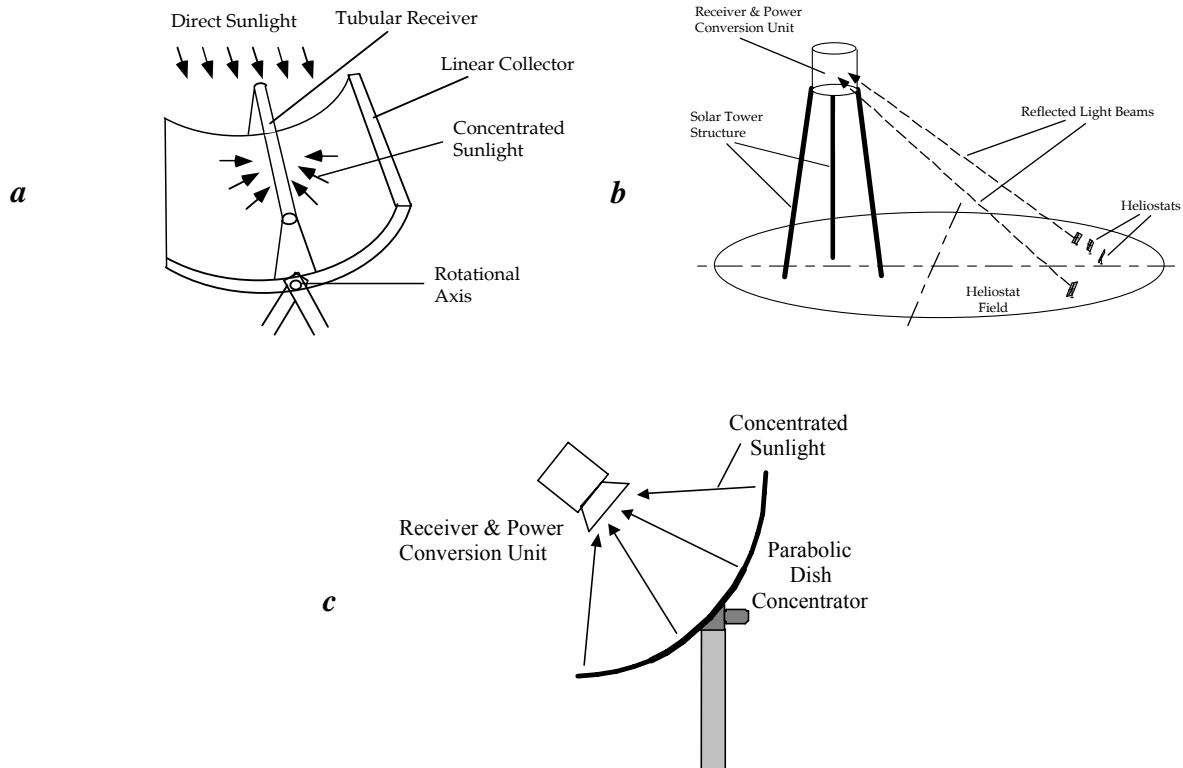


Figure 14 Three types of solar concentrators utilizing (a) linear collectors that focus on tubular receiver, (b) central receiver (solar power tower) with heliostat field that tracks the sun, and (c) on-axis tracking system with parabolic dish concentrator

On-axis Tracking Systems. On-axis systems, such as parabolic dish concentrators (Figure 14c), provide the highest optical efficiency of all the concentrating solar systems. Their main drawback is the concentrator size, which is limited by practical structural consideration. Recent progress in the development of small Brayton engines provides the option of using a dish/Brayton system as an alternative to the dish/Stirling system.

Estimates of large-scale (>50-MW) dish/Stirling facility costs are about \$2.5/W (Stoddard et al. 2005), although the current costs, based on several demonstration systems, are three to four times higher (Mancini et al. 2003). A recent study (Pitz-Paal et al. 2005) indicates that new developments in current areas of research can reduce cost by more than \$0.5/W. Other estimates, by Stirling Energy Systems (Stoddard et al. 2005), suggest even a larger potential cost reduction. The uncertainty in all of these estimates is considered to be large.

The development areas suggested in the Priority Research Directions should lead to the cost reductions required to make this technology competitive with conventional electricity production within five to ten years, assuming fossil fuels remain at present prices.

Solar Thermal to Electric Energy Conversion

Once the sunlight is concentrated by concentrators, several methods can be used to convert the heat into electrical energy. The conventional approach is to use a heat engine.

Several power conversion methods have been developed for solar central receivers. The power conversion unit of large central receivers (20–200 MWe) is likely to be a steam Rankine turbine, while smaller central receivers can have intrinsically better optics and thus accommodate Brayton and combined cycles operating at higher temperatures. A 10-MWe system using molten salt as heat transfer fluid and storage medium, combined with a steam Rankine turbine at up to about 850K, has been demonstrated in the U.S. Department of Energy's Solar II project. Other methods are (a) steam generation and superheating in the receiver, (b) heating atmospheric air to about 950K in the receiver and then using it to superheat steam, and (c) heating compressed air in the receiver to over 1100K and using it in a solar/fuel hybrid gas-turbine.

An important area that has not been sufficiently explored is the development of heat engines specifically designed for integration in a solar thermal system, as opposed to the customary approach of modifying existing engines. Such approach could take advantage of recent turbomachinery component developments (e.g., combustors, recuperators, alternators, bearings, ceramic rotors). The use of such engines instead of a modified existing fuel-driven engine should substantially simplify the power conversion unit, increase system efficiency, and lead to a significant cost reduction.

In general, new developments and innovations in the various methods described above can reduce the cost of solar thermal electricity production to about \$2/W, or even less (e.g., in dish/engines). Such installed costs are low enough to provide cost-competitive electrical energy if fuel costs remain at their present value and carbon emission limitations are implemented.

Solar Thermoelectric Power Generators. Direct thermal-to-electric energy conversion engines based on thermoelectric devices and thermophotovoltaic (TPV) energy converters provide new opportunities for medium power ranges that may rival direct photovoltaic (PV) power conversion and involve no moving parts.

Thermoelectric energy conversion technology, based on the Peltier effect and the Seebeck effect, exploits the thermal energy of electrons (and holes) for the energy conversion between heat and electricity, including power generation, refrigeration, and heat pumping.

A thermoelectric power generator has a maximum efficiency given by

$$\eta = \frac{T_h - T_c}{T_h} \frac{\sqrt{1 + ZT_m} - 1}{\sqrt{1 + ZT_m} + T_c / T_h}$$

where

T_h, T_c = temperatures at the hot and cold sides

THERMOELECTRIC MATERIALS AND DEVICES

Thermoelectric materials can be used in all-solid-state devices to produce electricity from hot sources. Figure 1 schematically represents how electricity can be generated for a heat source heated by a solar concentrator. With an appropriate thermal storage scheme, this could provide a 24-hour source of power. Efficient thermoelectric (TE) materials are usually semiconductors that possess simultaneously high electronic conductivity (σ), high thermoelectric power, and low thermal conductivity (κ). These properties define the thermoelectric figure of merit $ZT = (S^2\sigma/\kappa)T$; where T is the temperature. The $S^2\sigma$ product is often called the power factor. The quantities $S^2\sigma$ and κ are transport quantities and therefore are determined by the details of the crystal and electronic structure and scattering of charge carriers. Generally they cannot be controlled independently, however, the combination of new theories and experimental results suggests that they may be able to be decoupled to a significant degree. This raises potential new research opportunities for huge improvements in the figure of merit. State-of-the-art thermoelectric materials have $ZT \sim 1$. Recent developments on superlattices and nanostructured materials have led to the demonstration of ZT values of up to 2.4 (Figure 2). These nanostructured materials possess significantly lower thermal conductivity than their bulk counterparts, while having a power factor comparable to that of their bulk counterparts. With further research and development on thermoelectric materials and understanding of electron and phonon transport mechanisms (to achieve $ZT > 3$), thermoelectric converter efficiency up to 35% could be achieved.

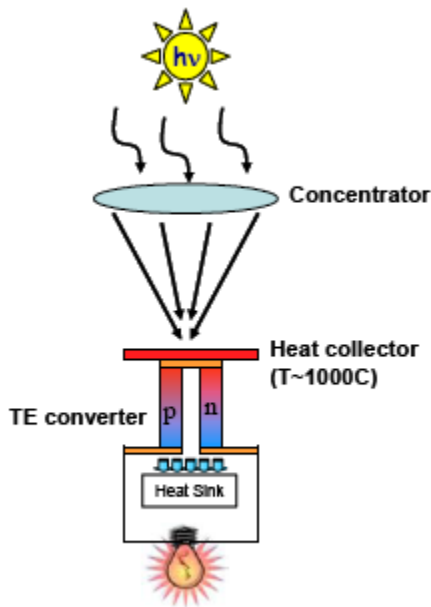


Figure 1 Illustration of a solar-thermoelectric power generator.

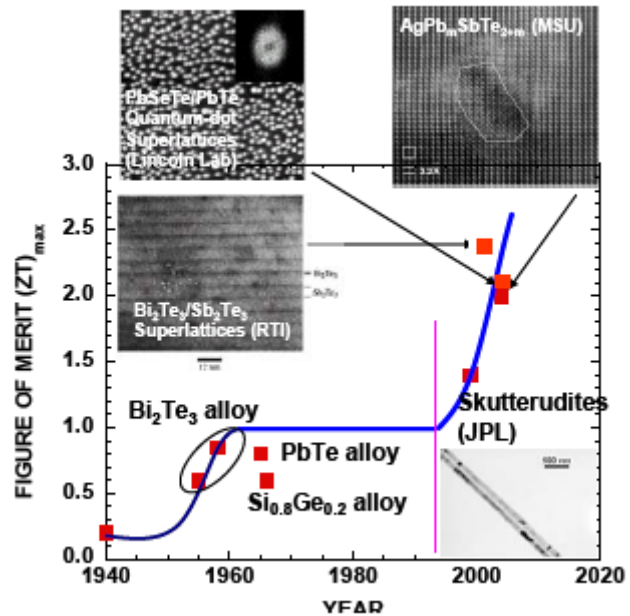


Figure 2 Progress timeline in thermoelectric materials.

T_m = mean temperature

Z = measure of the electronic power produced by the thermal gradient, divided by the thermal conductivity.

A large thermal conductivity would degrade performance. The product of Z and the working temperature T forms a nondimensional figure of merit, ZT . With a value of ZT between 3 and 4, thermoelectric devices would have an efficiency approaching that of an ideal heat engine. Thus, the key for the thermoelectric technology is to find materials with $ZT > 3$. Materials with reasonable ZT are often heavily doped semiconductors and some semimetals. The ZT value of a given material is temperature dependent; it usually peaks at certain temperature and drops off at higher temperatures.

The best commercial materials are alloys of Bi_2Te_3 with Bi_2Se_3 (n -type) and with Sb_2Te_3 (p -type). The alloys are used because the phonon thermal conductivity can be significantly reduced with only a small reduction in the electronic power factor. Bi_2Te_3 -based alloys have a peak ZT around 1 near room temperature. Thus, these materials are not optimal for solar power production, where the operating temperatures are higher. Bi_2Te_3 -based materials, used in some power generation applications, have a module efficiency that is limited to 5%. The U.S. National Aeronautics and Space Agency used SiGe alloys (and PbTe-based alloys) to make radioisotope-powered thermoelectric power generators operating in the temperature range of 300–900°C (and 300–600°C for PbTe-based alloys), with a system conversion efficiency ~6–7%. These materials all have a maximum ZT less than but close to 1.

Commercial thermoelectric materials, with a maximum $ZT \sim 1$, were mostly discovered in 1950s. Little progress was made in the subsequent years. In the 1990s, the possibility of improving the thermoelectric figure of merit based on electron band gap engineering and phonon engineering in nanostructures was investigated (Hicks and Dresselhaus 1993). These ideas have lead to a resurgence in thermoelectric research and significant progress in improving ZT , particularly based on nanostructured materials (Tritt 2001; Chen et al. 2003). Venkatasubramanian et al. (2001) reported that $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ -based p -type superlattices have a room-temperature ZT of 2.4. Harman et al. (2002) reported that PbTe/PbTeSe superlattices with nanodots formed by strain have a room-temperature ZT of 2.0. Hsu et al. (2004) reported bulk nanostructures of $\text{AgPb}_2\text{SbTe}_{2+m}$ with a ZT of 2.2 at 527°C. Meanwhile, several research projects aiming at improving device efficiency based on more mature materials are under way. The Jet Propulsion Laboratory reported a segmented thermoelectric uncouple with an efficiency of ~14% with the hot side at 975K and cold side at 300K. Solar thermoelectric power generators made of materials with $ZT \sim 4$ operating between room temperature and 1000°C would reach an efficiency of 35%. Given the impressive development made in the field of thermoelectrics over the past decade, the development of such materials seems to be a realizable goal.

Solar Thermophotovoltaics. Solar TPVs are similar to solar cells in that they convert photon energy into electricity. The fundamental difference from other PVs is that the photon source comes from a terrestrial thermal radiation emitter rather than directly from the sun. The radiation emitter can be heated by thermal sources such as fuel combustion or by concentrated solar radiation. Solar TPVs have a theoretical system efficiency of >30% for a concentration ratio of

>10,000. Compared with nonconcentrated solar PVs, the radiation emitted by the emitter has a higher power density. Thermal radiation from the heated radiation emitter has a longer wavelength and correspondingly, the PV cells used in a TPV system often have lower band gaps. Figure 15 shows a possible set-up of a solar TPV system. Concentrated solar energy raises the temperature of a solid thermal radiation emitter to a high temperature, typically to the range of 1,000–2,000°C. The efficiency of TPV systems depends critically on spectral filtering to avoid absorption of photons with energies below the band gap of the PV cells by parts of the system other than the emitter. The filtering elements can be free-standing or integrated in the emitter or the cells. The efficiency of a TPV power generator system can be roughly split into several factors:

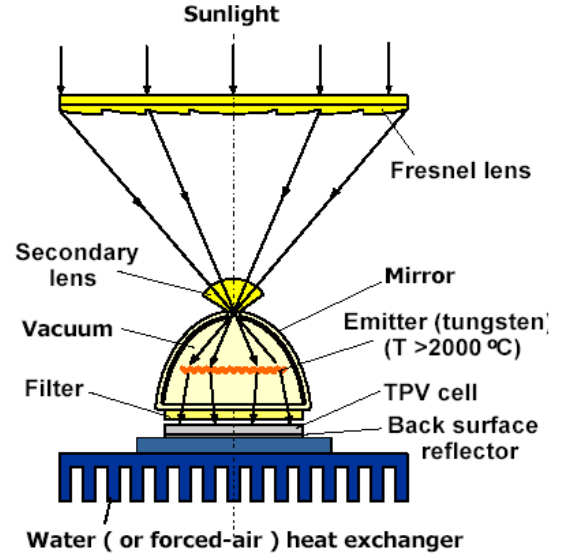


Figure 15 A possible set-up of a solar TPV system (courtesy: V.M. Andreev, IOFFE, St. Petersburg, Russia)

$$\eta = \eta_{\text{source}} \eta_{\text{spectral}} \eta_{\text{diode}} \eta_{\text{mech}}$$

where

η_{source} = efficiency of the conversion of the energy source (fossil, solar, nuclear) into thermal radiation from the emitter

η_{spectral} = combined efficiency of the emitter and filter that represents the fraction of photon energy above the band gap reaching the PV cell among all photon energy emitted

η_{diode} = efficiency of the PV cell converting the photon energy above the band gap into electricity,

η_{mech} = efficiency of converting PV cell electrical power output to the system power output that includes the energy lost in the pumping systems for fuel injection and thermal management.

Thermophotovoltaic energy conversion emerged in 1950s through the work of Henry Kolm at the Massachusetts Institute of Technology Lincoln Laboratory and a series of lectures given by Pierre R. Aigrain of the École Normale Supérieure (Nelson 2003). The focus of past work was on diode development and spectral control. Most diodes are built on antimony-based III-V materials with a band gap in the range of 0.4–0.7 eV (Wang 2004). One mature example is GaSb-based TPV diodes, which were also used in high-efficiency tandem solar cells. Thin-film-based diodes based on InGaAsSb are also extensively studied. The band gap of such thin-film materials can be tailored to match the heat-source temperature for optimum performance. Heterostructures can be used to further improve the cell performance. A 27% diode efficiency and 20% combined radiator-diode has been reported (Brown et al. 2003). With proper spectral

control and further diode developments, solar TPV systems with efficiency in the range of 25–35% are possible.

Spectral control is of crucial importance and holds the key for TPV efficiency. The goal of spectral control is to allow only photons above the band gap to reach the diode, as photons below the band gap not only represent a loss of useful energy but also reduce diode efficiency because they cause a rise in the diode temperature when being absorbed. For emission control, rare earth and transition metal-doped ceramics, refractory intermetallic coatings, thin-film and multilayer filters, plasmonic filters, and photonic crystals have been explored (Fleming et al. 2002; Licciulli et al. 2003). However, high-temperature operation of the emitters poses great challenges to the stability of the materials and structures. In comparison, filters, either stand-alone or built on the surface of the diode, suffer less from the stability issue.

In 2002, for a 1.5-kW GaSb-based system used as a home furnace, the total cost was estimated to be \$4,200 with \$2,700 for the furnace and \$1,500 for the TPV generator at ~15% efficiency (Fraas and McConnell 2002). This corresponds to \$1/W. If we add in the cost of the concentrator at \$1.6/W (assuming 15% efficiency, 850 W/m² solar insolation, and \$200/m² concentrator cost), the cost is \$2.6/W based on current technology (not counting other items that may be needed for the solar TPV system). If the efficiency is doubled to 30%, reducing the cost of energy in half, then the other major opportunity for cost reduction is the concentrator cost. This cost would need to be reduced significantly to bring the total cost to a target cost of \$1/W as for solar PV.

Concentrated Photovoltaics. Concentrated photovoltaic systems do not involve a solar thermal process, but they share the concentrator issues of linear and central receivers. Thus, this fast-developing field might well be considered under the “Crosscutting Areas” category. In this method, sunlight is concentrated by using mirrors or lenses, which are much cheaper than PV panels, and the concentrated light is focused onto the PV cells. The required cell area is therefore reduced by the concentration factor, which in present systems can be as high as 500; future CPV systems may be able to sustain even higher concentration ratios. We refer the reader to the Basic Research Challenges for Solar Electricity and Solar Electricity Technology Assessment for details of PV development. More details on CPV systems can be found in the Solar Thermal Technology Assessment in Appendix 1. Projections (Stoddard et al. 2005) put the long-term installed costs of CPV with multijunction cells currently under development at about \$2/W. The present cost of systems provided by Amonix and Solar Systems Pty Ltd. are roughly \$4/W; these systems use single-junction silicon cells and are in an early commercialization stage.

Concentrated Solar Thermochemical Processes

The concentrating component of these systems is identical to that of concentrated solar thermal processes for power generation, but the energy conversion is a thermochemical process converting radiation-to-heat-to-chemical potential. These systems provide an effective means for long-term storage and transportation of solar energy (e.g., in the form of fuel) and its utilization in motor vehicles and industrial applications. The basic concept is shown in Figure 16.

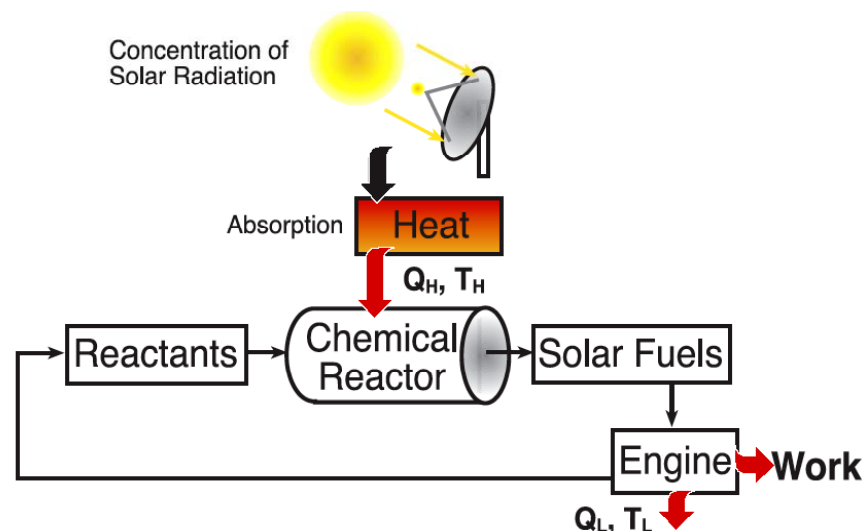


Figure 16 General concept of solar-driven thermochemical cycle

Water-splitting Thermochemical Cycles. In recent years, significant progress has been made in the development of optical systems for large-scale solar concentration capable of achieving mean solar concentration ratios exceeding 2,000 suns (1 sun = 1 kW/m²), and present efforts are aimed at reaching concentrations of 5,000 suns. Such high radiation fluxes allow the conversion of solar energy to thermal reservoirs at 2000K and above, which are the conditions needed for efficient water-splitting thermochemical cycles using metal oxide redox reactions. This two-step cycle consists of first-step solar endothermic dissociation of a metal oxide and second-step nonsolar exothermic hydrolysis of the metal. The net reaction is $\text{H}_2\text{O} = \text{H}_2 + 0.5\text{O}_2$, but since H_2 and O_2 are formed in different steps, the need for high-temperature gas separation is thereby eliminated.

Solar Thermal Decarbonization Processes. Hybrid solar/fossil endothermic processes, in which fossil fuels are used exclusively as the chemical source for H_2 production and concentrated solar power is used exclusively as the energy source of process heat, offer a viable route for fossil fuel decarbonization and create a transition path toward solar hydrogen. An important example of such hybridization is the endothermic steam gasification of carbonaceous materials (coal, coke, biomass) to syngas. The advantages of supplying solar energy for process heat are threefold: (1) the calorific value of the feedstock is upgraded; (2) the gaseous products are not contaminated by the by-products of combustion; and (3) discharge of pollutants to the environment is avoided. A Second-Law analysis for generating electricity by using solar gasification products indicates the potential of doubling the specific electrical output and, consequently, halving the specific CO_2 emissions compared with conventional coal-fired power plants.

Another approach to hydrogen production is high-temperature electrolysis of water in a one-step process or electrolysis of another material as part of a two- to four-step water-splitting process.

An overview of solar thermochemical processes is provided by Steinfeld and Palumbo (2001). Some topics addressed by recent studies are

- Evaluation of novel processes for fuel synthesis (Möller et al. 2002; Dahl et al. 2004) and material production (Murray et al. 1995; Wieckert et al. 2004);
- Development of novel solar reactors (Anikeev et al. 1998; Osinga et al. 2004); and
- Catalyst development for solar-driven high-temperature gas-gas reactions (Berman and Epstein 1997).

The development of fuel production using solar energy is in a relatively early stage. Progress in the above topics is crucial to assess the technological viability of such processes prior to estimates of their economical feasibility.

Present long-term projections suggest that the solar fuel production processes described above will probably be two to three times more expensive than present high-emission industrial methods. However, they also predict that solar fuel production can be competitive if carbon emission cost is considered (Steinfeld and Palumbo 2001).

Low-temperature Solar Thermal Systems

Low-temperature solar thermal systems have the potential to supply a significant number of U.S. households and commercial buildings with heating, cooling, and refrigeration; refer to the Solar Thermal Technology Assessment for further details. To overcome the current barrier of high initial cost, there is a need for new materials in a number of roles. Durable polymeric materials or films are sought that provide high transmittance in the visible spectrum and protection from ultraviolet light, which is crucial in the successful development of polymer collectors (Davidson et al. 2002). The viability of polymer heat exchangers and absorbers depends on the development of extrusion-grade thermoplastic polymers with high strength to minimize the required thickness of the polymer structure and resistance to hot chlorinated water.

Low-cost methods to improve the thermal conductivity of polymers are desirable. Some methods are proposed by Danes et al. (2002) and Davidson et al. (2002), but further work is required. An understanding of the mechanism leading to crystal growth on polymeric surfaces is required to develop strategies to avoid such growth. Of key interest are chemical differences between polymers, which influence their interaction with water; the mechanism of calcium carbonate nucleation; and scale morphology and structural differences (e.g., surface roughness), which may affect calcium carbonate nucleation and adhesion (Sherman 2001; Wang et al. 2005).

Other needs are found in the development of low-temperature solar thermal systems that can supply both hot water and space heating. Cost-effective thermal storage is sought for seasonal or annual rather than daily energy requirements. Chemical or phase-change materials may provide performance superior to that of water-based storage options. Initiatives to develop systems that are part of the building envelope should be supported for both existing and newly constructed buildings. The solutions will be different. New buildings represent an opportunity for major

innovation by incorporating the solar systems into roof and wall. Combined solar thermal and PV systems, both concentrating and nonconcentrating configurations, that produce electricity and heat should be investigated, in particular for integration into the building envelope.

BASIC SCIENCE CHALLENGES, OPPORTUNITIES, AND RESEARCH NEEDS

Materials hold the key to the thermal utilization of solar energy. High-efficiency thermoelectric and TPV converters coupled to solar concentrators have the potential to generate electricity at converter efficiencies from 25 to 35%. Currently, terrestrial thermoelectric and TPV systems are mostly based on combustion heat, and solar-based thermoelectric and TPV systems have not been systematically investigated. However, concentrator-based thermoelectric and TPV systems have advantages over combustion systems as the heat loss from combustion exhaust is eliminated in solar concentrator systems. Solar concentrators and hot-water heaters call for new low-cost polymer-based materials and composites. Significant progress has been made in these areas over the last decade, particularly by exploiting nanoscience and nanotechnology. Further fundamental research should target developing thermoelectric materials with ZT up to 4, selective thermal emitters that can withstand $>1,000^{\circ}\text{C}$ and the development of polymer-based materials for use in heat transfer and as structural materials.

Research in thermochemical fuel production is aimed at the advancement of the thermochemical and thermoelectrochemical sciences applied in the efficient thermochemical production of solar fuels, with focus on solar hydrogen production. Concentrated solar radiation is used as the energy source of high-temperature process heat for endothermic chemical transformations. Research emphasis should be placed on (1) the fundamental analysis of radiation heat exchange coupled to the kinetics of heterogeneous thermochemical systems, (2) the design of advanced chemical reactor concepts based on the direct irradiation of reactants for efficient energy absorption, (3) the development of high-temperature materials ($T > 1,500^{\circ}\text{C}$) for thermochemical and thermoelectrochemical reactors, and (4) the production of hydrogen by water-splitting thermochemical cycles via metal oxide redox reactions and by thermal decarbonization of fossil fuels via gasification of carbonaceous materials.

Thermoelectric Materials

High-efficiency thermoelectric converters coupled to solar concentrators have the potential to generate electricity at converter efficiencies from 25 to 35%. The primary challenge to achieve these efficiencies is the development of new, high-efficiency thermoelectric materials with thermoelectric figures of merit $ZT > 3$. The approach is to develop new classes of materials by using a combination of exploratory synthesis and transport properties characterization guided by theoretical efforts.

Comprehensive Theoretical Guidance on Thermal and Electronic Transport in Complex Structures. Over the past decade, progress has been made in the theory of thermoelectricity, notably the quantum size effects on the electronic power factor (Hicks and Dresselhaus 1993), interface effects on thermal conductivity (Chen 2001), and the use of density functional theory

for electron and phonon band structures (Sing 2001). However, existing theoretical approaches lack predictive power. For bulk materials, the challenges lie in predicting the structures of materials, and their electronic and phononic band structures and transport properties, and in understanding the impact of defects in the materials on transport properties. For nanostructured materials, a crucial issue is the role of interfaces on electron and phonon transport. Although the ultimate goal should be set at predictive tools, modeling should help in pointing directions for materials synthesis and structural engineering. Insights gained through combined theoretical and experimental studies on fundamental thermoelectric transport processes are invaluable in the search of high-ZT materials.

New High-performance Bulk Materials. Several new bulk materials that demonstrate $ZT > 1$ have been identified over the last 10 years. Diverse classes of potential materials need to be developed so they may serve as sources for novel high-ZT compounds. Mechanisms for decoupling electron transport from phonon transport in such materials through modification need to be identified. Research opportunities along these directions need to be systematically pursued.

Nanoengineered Materials. Nanoscale engineering may be a revolutionary approach to achieving high performance bulk thermoelectric materials. Recent results in bulk materials (based on AgPbSbTe, called LAST) have shown $ZT > 2$ in a bulk thermoelectric material (Hsu et al. 2004). An intriguing finding is that this material exhibits a nanoscale substructure. Given the former successes for high ZT in nanomaterials (quantum dots and superlattice materials), the nanostructure observed in the LAST material may be essential for achieving a $ZT > 2$. Therefore, one approach to nanoscale engineering is to synthesize hybrid or composite materials that have nanoscale thermoelectric materials inserted into the matrix of the parent thermoelectric material. Developing synthetic processes to nanoscale substructures is an important undertaking.

Nanoscale thermoelectric materials that can independently reduce phonon transport without deteriorating electronic transport have been implemented in $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ superlattices (Ventakatasubramanian et al. 2001) offering $ZT \sim 2.4$ at 300K and quantum dot PbTe/PbTeSe superlattices (Harman et al. 2002) offering $ZT \sim 2$ at 550K. Most of the enhancements have been attributed to lattice thermal conductivity reduction in nanoscale dimensions. It is anticipated that further reduction is possible with a comprehensive understanding of phonon transport in low-dimensional systems. There is also potential for significant ZT enhancement through quantum-confinement effects (Hicks and Dresselhaus 1993).

Thermophotovoltaics

Significant progress has been made in TPV cells (Coutts et al. 2003; Aicher et al. 2004). The efficiency of TPV systems depends critically on spectral control so that only useful photons reach the PV cells. Ideally, spectral control should be done at the emitter side, although filters standing alone or deposited on PV cells are also being developed. However, emitter temperatures exceeding 1000°C impose great challenges on the stability of the materials and structures used in a TPV system, especially for those components that provide spectral control. Photonic crystals (Fleming et al. 2002), plasmonics, phonon-polaritons, coherent thermal emission (Greffet et al.

2002), left-handed materials, and doping with lanthanides are concepts from the optics community which can be exploited for the spectral control components required in TPV systems.

Key research needs are as follows:

- ***Nanostructured metallic and dielectric materials with low diffusion and evaporation rates:*** The major challenge of spectral control for TPV systems is given by the high operating temperatures of $\sim 1,200^{\circ}\text{C}$ in the case of fuel-powered TPV and $\sim 2,000^{\circ}\text{C}$ in the case of solar TPV. Diffusion processes and evaporation of material may limit the durability of the components significantly. Suitable concepts of material engineering to reduce these effects have to be developed and fully understood by using multiscale models.
- ***Scalable manufacturing processes applicable to various geometries:*** The optical approaches mentioned are based on materials properties and on precise nanostructuring of the materials. Currently, the techniques for producing nanostructures are top-down approaches that are limited to small homogeneously structured areas and to flat surfaces. They are also not cost-efficient. Thus, novel manufacturing techniques need to be developed, and these very likely will incorporate self-organization processes.
- ***Novel device concepts:*** Novel device concepts such as microgap TPV and device structures should be explored. Tunneling of evanescent and surface waves can lead to devices with higher power density and efficiency. Technological challenges to maintain the gap in the range of 10 nm to submicrons in high-temperature systems must be solved for such concepts to be useful in practical systems.

Solar Concentrators and Hot-water Heaters

Today's concentrators generally consist of a precisely shaped metallic support structure and silver-glass reflector elements with an average reflectivity of 88%; they are responsible for more of 50% of the investment cost of concentrating solar systems. Likewise, the primary challenge for widespread implementation of nonconcentrating solar thermal systems is to substantially reduce the initial cost of installed systems. Future research should aim at a paradigm shift from metal and glass components to integrated systems manufactured by mass production techniques, such as those associated with polymeric materials. The major limitations of currently available polymers are associated with their inability to withstand outdoor elements, such as ultraviolet radiation, water and oxygen exposure, and mechanical and thermal stresses, for at least 20 years. Needs include development of thin-film protection layers for reflectors; high-strength, high-thermal-conductivity polymers; materials with high transparency and durable glazing for heat exchangers; and engineered surfaces that prevent dust deposition on reflector surfaces.

Heat transfer surfaces for water heaters call for polymer and composites with high mechanical strength, ultraviolet degradation resistance, and high thermal conductivity. Concentrator support structures require polymers with high mechanical strength and low thermal expansion

coefficient. The thermal conductivity of most polymers is 0.2–0.4 W/m-K. A hundred- to thousandfold increase in thermal conductivity is needed to make polymers competitive. New composite materials hold the promise of high mechanical strength and high thermal conductivity.

Surface modifications are needed for photon and thermal management. High-efficiency solar absorbers for water heaters can be formulated to exploit the concept of photonic crystals. Mirrors and glass that repel dirt can significantly increase efficiency and reduce cleaning cost. Surface engineering is also needed to prevent scale formation in solar thermal heat exchangers. Fundamental research on particle-surface interactions and solid precipitation and deposition processes can help solve these challenges.

Solar Thermochemical Fuel Production

Radiative Exchange in Chemically Reacting Flows. Fundamental research, both theoretical and experimental, is needed in radiation heat transfer of multiphase chemical reacting flows. The analysis of thermal radiative transport coupled to the reaction kinetics of heterogeneous chemical systems, in which optical properties, species composition, and phases vary as the chemical reaction progresses, is a complex and challenging problem to be tackled in the design of high-temperature thermochemical reactors. Of special interest is the radiative exchange within absorbing-emitting-scattering particle suspensions, applied in thermochemical processes such as thermal cracking, gasification, reforming, decomposition, and reduction processes.

Directly Irradiated Solar Chemical Reactors. The direct absorption of concentrated solar energy by directly irradiated reactants provides efficient radiation heat transfer to the reaction site where the energy is needed, bypassing the limitations imposed by indirect heat transport via heat exchangers. Spectrally selective windows can further augment radiation capture and absorption. The use of nanoparticles in gas/solid reactions augments the reaction kinetics and heat and mass transfer.

Materials for High-temperature Solar Chemical Reactors. Materials for construction of solar chemical reactors require chemical and thermal stability at temperatures $>1,500^{\circ}\text{C}$ and solar radiative fluxes $>5,000$ suns. Advanced ceramic materials and coatings are needed for operating in high-temperature oxidizing atmospheres and for withstanding severe thermal shocks occurring in directly irradiated solar reactors.

The ability to develop electrolysis processes at high temperatures depends on the development of structural materials that are stable at $T > 800^{\circ}\text{C}$ and other materials that can be used for various components, such as absorbers, electrolytes, and electrodes of the solar reactor and electrolysis units

The development of high-temperature materials for solar reactors is in a relatively early stage. Progress in the above topics is crucial in assessing the technological viability of such processes prior to estimates of their economical feasibility.

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CROSS-CUTTING RESEARCH CHALLENGES

BACKGROUND

Rapid developments in nanoscience and the revolution in biomedical research have combined to create an unusual opportunity for advances in basic solar energy research. Because the individual microscopic steps of solar energy use take place on the nanometer scale, the ability to pattern and control matter on this length scale presents unusual opportunities for researchers to create new materials for solar energy conversion and use. The emergence of new fundamental physical properties on this length scale could potentially lead to far more efficient technologies for conversion of solar energy to electricity and fuels. To take advantage of these new materials and processes, researchers must create complex arrangements of nanoscale components, like those that occur throughout biological systems. It may be possible to directly employ living systems to create fuels; alternatively, biological macromolecules may be used to direct the assembly of nanoscale artificial building blocks. Artificial approaches to system assembly of nanoscale components will benefit from incorporating the features — including fault tolerance — of biological systems.

Low-dimensional Materials and Solar Energy

Specific patterns of matter on small length scales can be used to control the energy distribution, or *density of states*, of fundamental excitations associated with light (photons), electrical charge (electrons), and atomic vibrations such as sound and heat (phonons).

Patterns on the length scale of the wavelength of light can be used to manipulate photons. Spontaneous absorption and emission rates are directly proportional to the photon density of states, so this capability can play a wide-ranging role in almost all solar utilization technologies. Photon management, in this case, leads to systematic manipulation of the wavelengths at which light is absorbed or emitted.

Patterns of matter on the length scale of the wavelength of electrons allow for the control of the density of electronic states, as well as the density of phonon states. In such “quantum-confined” systems, both optical and electrical properties can be widely tuned. Quantum dots and rods may play a key role as the absorbers of light in future-generation solar converters. The wavelength range of absorption can be widely adjusted. More importantly, fundamental relaxation processes, which lead to energy losses in bulk materials, can be adjusted in nanostructures — offering the promise of more efficient light absorption and energy transfer. Nanowires may serve as the conduits for the transport of charges. In one-dimensional nanostructures, it is possible to adjust the length scale for electron scattering. In the harvesting of charges, the use of materials with ballistic transport of carriers can reduce losses. The phonon scattering rate is enhanced in one-dimensional superlattices so that the thermal and electrical conductivity can be separately tuned — which is the key to creating improved thermoelectrics.

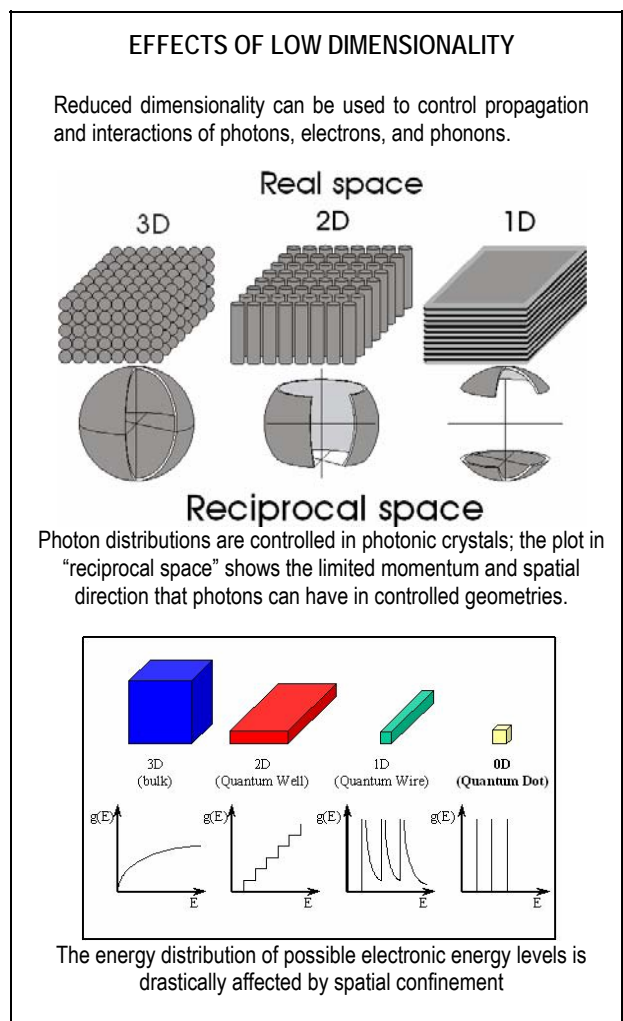
A key feature of all nanoscale materials is the presence of multiple interfaces between different components. To realize the benefits of nanoscale patterning, researchers need to systematically investigate the transport of charges and molecular species across these interfaces. This issue has been of particular concern in the case of electrical contacts.

System Assembly and Defect Tolerance

To realize the potential of nanoscale-based solar conversion, the chemistry of molecular and material synthesis and assembly must be further elucidated. The synthesis of complex molecules, macromolecules, and nanoparticles is an underlying tool that continues to evolve in important ways. The key limiting issue now is the merging of these component building blocks into functional assemblies and, ultimately, into complete systems. This capability requires improved understanding of the organic-inorganic hard-soft interfaces, as well as the ability to harness multiple weak interactions to create designed patterns. This is how biological materials are organized on length scales larger than those of individual macromolecules, yet it remains very challenging for chemists and materials scientists working with artificial components. It is important for researchers to emulate many features of biological system assembly, chief among them (1) the ability to create advanced materials despite the presence of disorder and defects and (2) the ability not only to assemble components, but also to disassemble and reassemble them. These capabilities are essential for creating advanced solar converters that combine high performance with low cost.

New Experimental and Theoretical Tools

Progress in the field of solar energy depends critically on the development of new tools for the characterization of matter and on new theoretical tools. On the experimental front, one major goal is to create probes that can reveal the structure and composition of nanoscale materials with atomic resolution. A second goal involves development of tools that can be used to follow the complete flow of energy through each primary step of the solar conversion processes — from absorption, to charge transfer, transport, harvesting, and chemical conversion and separation. Theoretical tools are also needed to aid in the understanding of these elementary steps. The wide



range of time and length scales spanned by these phenomena poses a significant theoretical challenge. The ability to compute the properties of systems with 1,000 to 10,000 atoms will permit modeling of complex problems, such as the electrochemical behavior of molecule-nanocrystal systems, catalytic hydrogen production, and biological light-harvesting systems. In addition, there is a significant need to create “inverse tools,” which receive a wide range of simultaneous desired properties as inputs and yield materials arrangements as outputs.

Specific areas requiring improved understanding to enable significant progress in any approach to solar energy include photon management, carrier excitation, charge transport, energy migration, and interface science. The challenges in each of these areas are outlined below.

ENHANCED PHOTON MANAGEMENT

Two primary steps are common to all solar energy architectures: the guidance of sunlight to a target and the absorption of this radiation. Solar energy converters must first be able to harvest sunlight and channel the photons with minimal energy loss to an appropriate receiver. Optimal use of the sunlight then requires a match of the solar spectrum to the absorption spectrum of the solar converter. The design of new solar energy systems — whether photovoltaic (PV), photocatalytic, or based on other approaches — must consequently be matched to high efficiency in these primary processes of photon collection and absorption.

Recent scientific advances suggest several promising new approaches to these challenges, which we collectively term “photon management.” Progress in materials and nanoscale optics has the potential to greatly impact the design of light-collection technologies. It has long been known that sharp features can concentrate electric fields. The corresponding physical phenomenon for electric fields of the rapidly varying optical radiation can be achieved with elements structured on the nanometer length scale (Figure 17). Such schemes have led to electric fields sufficient to allow enhancement of normally weak Raman cross-sections to a level at which spectroscopy of individual molecules has been demonstrated (Nie and Emery 1997). A related technique uses surface plasmons to channel and concentrate electric fields (Hutter and Fendler 2004). Such approaches, in which electric fields can be significantly enhanced, might also enable nonlinear (or multi-step) optical processes to play a role in future solar energy conversion schemes. Other approaches for photon management include the creation of novel photon up-converters and down-converters to achieve better matching of the solar spectrum with the electronic excitations in the solid (Trupke et al. 2002). For example, an up-conversion design might involve the use of intermediate band states in semiconductors that allow the sequential absorption processes of lower-energy photons to produce a higher-energy excitation (Cuadra et al. 2004).

Photon management might also take a biomimetic approach, for which the light-harvesting techniques found in natural systems provide guidance (Scholes 2003; Diner and Rappaport 2002; Chitnis 2001). Other areas in which new approaches might emerge include the use of materials exhibiting a negative index of refraction (Pendry 2000) or the use of highly scattering materials to localize photons (Ziegler 2003).

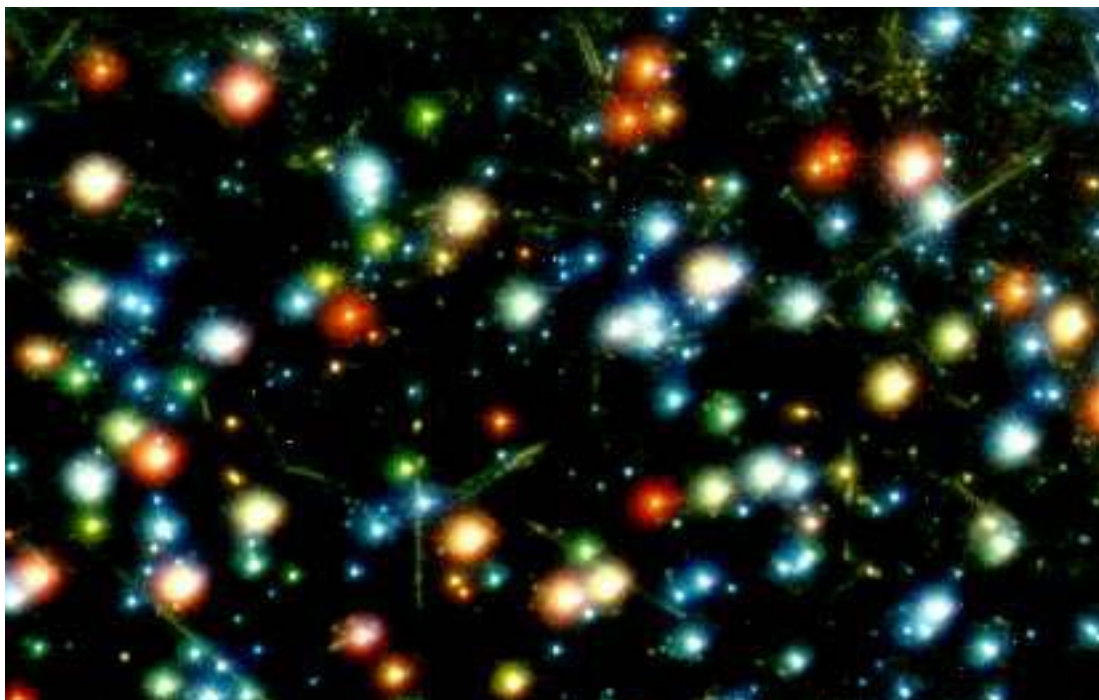


Figure 17 Control of light fields using metallic structures. Recent advances have permitted the concentration of light on a very fine length scale by using nanoscale structures. The figure shows an experimental image of white light scattering from silver nanoparticles. The color differences arise from the limits imposed by particle shape on the interactions of light and electrons within a nanoparticle. Enhancements in the light intensity exceeding 1,000 times can be achieved by using appropriately shaped nanostructures, as has been demonstrated by single-molecule Raman scattering and other enhanced optical effects. (Source: Michaels, Nirmal, and Brus 1999)

Photonic crystals are periodic structures — analogous to the usual crystals formed of atoms — that can be tailored to modify the propagation of light (Johnson and Joannopoulos 2002). Researchers have recently identified and demonstrated many fascinating properties of these systems, including new schemes for light guidance and localization. Photonic crystals may be applied to solar energy conversion in a variety of ways, starting with the production of highly effective optical filters, anti-reflecting coatings, and mirrors that exhibit engineered responses as a function of the angle of incidence. Photonic crystals can also channel the light to areas where the absorbing molecules are located. The interaction of the photonic cavity with the absorption material may also be a mechanism to control the absorption properties of the absorbing material. A promising approach to tailoring the absorption properties of materials is through control of dimensions on the nanoscale. The well-known quantum size effects in nanoparticles are only the first example of nanoscale control of the optical properties of materials (Alivisatos 1996; Empedocles and Bawendi 1999). Multi-component systems could enable another level of sophistication in the design of optical properties (Wu et al. 2002; Redl et al. 2003).

Research Issues

Advances in the synthesis of high-quality novel materials ultimately underlie potential progress in both photon management and the control of optical absorption. Giant field enhancements will require materials with controlled properties on the nanoscale, as well as new capabilities for assembling these components into precise nano-optical structures. Potential photon up-conversion or down-conversion schemes will require new semiconductor materials with carefully controlled electronic transitions that provide intermediate band states. In addition, advances in plasmonic waveguide development will require new approaches to the synthesis and fabrication of high-quality nanoshaped structures. Finally, new hard and soft materials must be developed with controlled absorption, reflection, and emission properties. For certain applications, like thermo-photovoltaics, high-temperature stability is also an important issue. Photostability is a ubiquitous issue for all solar energy conversion schemes.

The science of electric-field concentration in nano-optical structures is not fully developed. Theoretical and experimental investigations are needed to establish a full understanding of the field enhancement in nanostructured optical systems and to develop an optical design methodology for these systems, analogous to what is now available for conventional optical elements (Figure 18). The use of surface plasmon-polariton waves to capture and deliver energy to target receptors is a promising approach, but further research is needed to understand and optimize such (energy capture and delivery) processes. The use of photonic-band-gap structures requires a deeper understanding of the interaction of the photonic structure with the solar energy conversion target.

Research opportunities also exist in establishing a more complete understanding of what controls optical absorption in light-harvesting biological systems composed of complex ensembles of chromophores, as well as in studying and developing analogous constructs using hard materials, such as nanoparticles. General principles for self-consistent design of the photon control, optical absorption, and subsequent solar energy conversion steps must be established.

Impact

The primary processes of photon delivery, in terms of both spatial and spectral distribution, and optical absorption are common to all approaches to solar energy conversion. Advances in photon management and the tailoring of optical absorption properties can consequently impact the efficiency of any solar energy scheme.

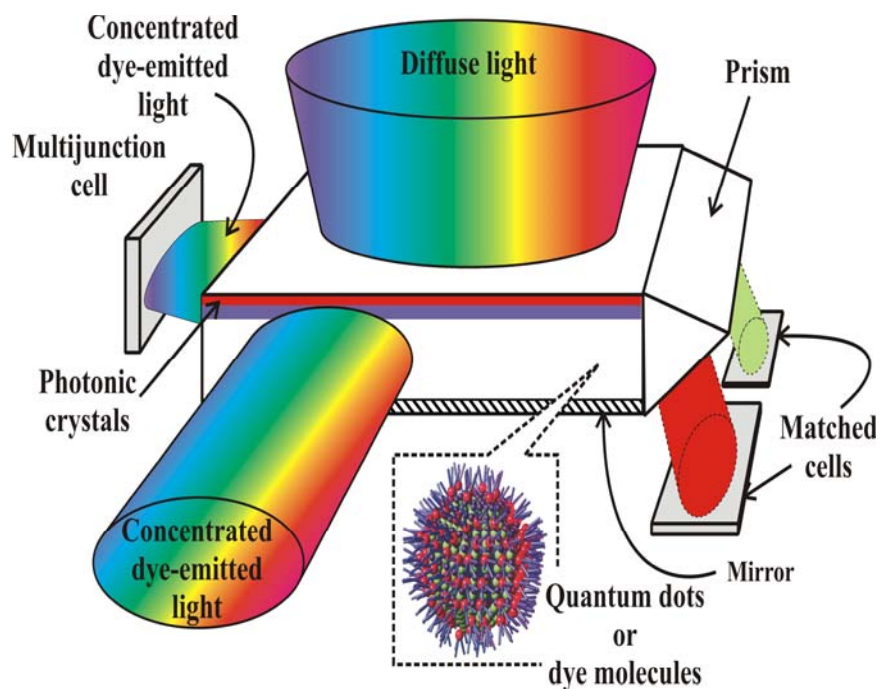


Figure 18 Concentration of sunlight provides significant advantages for many schemes of solar energy conversion. While traditional methods using mirrors have been developed, new approaches suitable for large areas are critical. The figure depicts a concentrator that makes use of photonic crystal filters (top of collector) and quantum dots or dye molecules (solution between plates) to achieve large-area light collection. (Source: FULLSPECTRUM undated)

CONTROL OF CARRIER EXCITATION, CHARGE TRANSPORT, AND ENERGY MIGRATION

Many of the limitations in solar energy use are imposed by the efficiency limits of elementary physical processes. Most broadly, these processes include (1) the absorption of a photon from the solar spectrum, (2) the transport of the charge carriers or energy from the absorption site to a site where it can be used (e.g., a heterojunction where excitons are split into separate electrons and holes), and (3) the conversion of the excitation energy to drive the desired process (e.g., electrical current or a chemical reaction). Complex interactions determine the efficiency of these steps. Scattering processes can limit carrier transport, but on certain length scales, such transport can also be ballistic. Excitons created by absorption of light can diffuse, but they are also subject to radiative relaxation processes. Heterogeneous media, interfaces, defects, and disordered homogeneous materials can also trap excitons and carriers. Further, it may be possible to control the flow of energy among various competing paths, as natural systems that harvest solar energy through photosynthesis do. Current research frequently takes an empirical approach, surveying available materials and selecting those with the best parameters. However, revolutionary progress in solar energy utilization would be possible if we had a sufficient understanding of the relationship between materials structure and function. Such an understanding would enable the rational design of structures that would provide detailed control of the elementary processes of carrier excitation, charge transport, and energy migration.

Advances across several science frontiers suggest new approaches that could enable such rational design, particularly for low-dimensional and tailored multi-component materials. Controlling the size and dimensionality of the structures on the nanoscale would allow scientists to modify the density of electronic states, as well as of phonons (Alivisatos 1996; Empedocles and Bawendi 1999; Cahill et al. 2003). In addition, entirely new processes may emerge that expand our view of how solar energy systems can be designed. One example is the recent discovery of efficient carrier multiplication in the photo-excitation of semiconducting quantum dots (Schaller and Klimov 2004). The formation of multiple excitons following the absorption of a single photon can reduce the loss of energy to heat that usually accompanies carrier relaxation to the band edge and otherwise places fundamental limits on the efficiency of PV solar energy conversion (Werner et al. 1994). While the design of structures with optimized properties for the control of carrier excitation, charge transport, and energy migration remains a challenging problem, recent advances in the synthesis and assembly of high-quality multi-component and hybrid nanostructures, in concert with advances in our ability to probe and understand the relationship between structure and function in model systems, offer a realistic path to achieving this goal.

Research Issues

The ability to synthesize high-quality samples of novel materials forms the foundation for progress toward the goal of rational design. The promise offered by the control of elementary processes is suggested particularly in low-dimensional and multi-component materials. It has long been understood that while the absorption spectra of semiconductor quantum dots are tuned by the confinement size (Alivisatos 1996; Empedocles and Bawendi 1999), the ligand fields surrounding the quantum dots also affect absorption spectra and excitation lifetimes (Murray and Kalyuzhny 2005). Although nanoscale synthesis research efforts are well underway (O'Brien and Pickett 2001), the ability of scientists to control the composition, shape, morphology, and quality of nanostructured materials is still inadequate. Synthesis of high-quality, multi-component nanomaterials is one example. Such multi-component structures could provide heterogeneous band-gap junction structures that are critical for PV applications, but with controlled excitation lifetimes. Another opportunity lies in the synthesis of hybrid materials, including those with controlled interfaces between hard and soft materials, where the advantages of each are exploited in the resulting hybrid (Wu et al. 2002). The synthesis of a wide variety of novel materials is essential to enable the rational design of solar energy materials with controlled elementary processes.

The synthesis of high-quality materials must be coupled to the development and exploitation of new characterization tools capable of resolving elementary physical processes at appropriate length and time scales and with sufficient energy resolution. This effort must include (1) the development of laboratory tools and techniques, such as optical techniques to probe carrier dynamics on ultra-fast time scales; and (2) the improvement of electron-microscopy techniques to allow higher resolution and larger working distances for in situ transmission electron microscopy (TEM) studies. On another scale, the effort requires the development of national facilities to provide new tools, such as advanced synchrotrons to probe solar material nanostructures with greater energy and spatial resolution. Given the complexity of the materials and the underlying physical processes, it is critical to have an array of experimental tools that can probe the diverse properties that control the functionality of novel materials.

Another critical research need for the design of structures that control carrier excitation, charge transport, and energy migration is the promotion of theoretical studies that can provide a deeper understanding of the observed relationships between high-quality materials structure and function and guide the discovery of new approaches. These studies would involve both greater computational effort and advanced analytic theories describing the behavior on a range of length and time scales, as well as within and between various biological, organic, and inorganic materials.

Impact

Progress in the rational design of structures that control carrier excitation, charge transport, and energy migration would enable revolutionary advances in solar energy utilization. Such advances would change the way scientists approach the problems of optimizing efficiency in solar energy conversion systems. Anticipated advances include a significantly improved use of the solar spectrum, with reduced loss to dissipative processes. In addition to optimizing elementary processes for existing solar energy designs, researchers are expected to develop entirely new approaches that exploit new scientific advances. This approach is illustrated with the recently discovered phenomenon of carrier multiplication, an advance that enables quantum efficiencies for carrier generation exceeding 100%. This phenomenon also suggests new approaches to solar-driven photochemical processes that require multiple oxidation/reduction steps by eliminating the need to store charge from sequential single-photon/single-electron steps.

INTERFACE SCIENCE OF PHOTO-DRIVEN SYSTEMS

Interfaces are integral to most schemes for solar energy conversion, including solar generation of electricity and fuels and thermoelectrics. For these technologies, the successful control of the properties of interfaces between dissimilar materials is essential. Mechanical stability, charge separation, and charge transfer depend upon detailed atomic configurations, interfacial chemistry, and electronic coupling. Interfaces can be solid-solid, liquid-solid, and liquid-liquid and include both bulk-like junctions and junctions between nanomaterials and solids, polymers, molecules, and solvents. Organic-inorganic material junctions are also expected to play a role in solar conversion technologies.

The prevalence and importance of interfaces, as well as the serious difficulties that their control often imposes, can be easily understood by reference to a few of the critical underlying technical issues. An issue of broad importance is that of electrical contacts. This challenge arises in all PV approaches to solar energy in which solar energy is removed from the device in the form of electrical current. A particularly challenging issue concerns transparent conductors (Ohta et al. 2003; Wu 2004), which are vital for most implementations of PV devices (Figure 19). Another common bottleneck in the exploration of new materials lies in making reliable contacts of low resistance. Interfaces are also critical with respect to carrier trapping and recombination processes that often significantly decrease the efficiency of PV devices. The role of interfaces is, of course, even more critical in the new approaches that use nanostructured materials (O'Brien and Pickett 2001) because of their enhanced ratio of interface-to-bulk material.

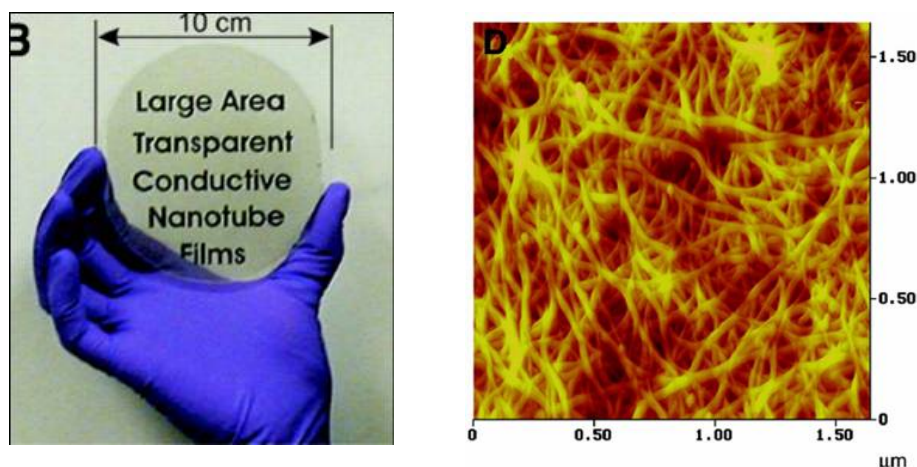


Figure 19 Transparent conductive electrodes represent one of the major challenges for PV devices. The problem involves both the bulk properties of the electrode material and its interface with the PV media. The figure shows the progress achieved in developing a new transparent conductive electrode material based on carbon nanotubes. (Source: Wu 2004)

While PV devices typically comprise thin films with important interfacial components, some schemes are *inherently* interfacial in character. This is the case in dye-sensitized devices, in which photoexcitation and exciton breaking occur at the interface between two distinct media (O'Regan and Grätzel 1991). It is clear that the efficiency and reliability of such devices is determined, to a large degree, by physical and electronic structure at the interface, by the dynamics of charge separation, and by the desired and side oxidation/reduction reactions at the interface. A further important example of a solar energy conversion scheme that is inherently dominated by interface characteristics is the photocatalysis process for solar fuel production (Hermann 2005). In this process, photo-driven heterogeneous catalysis is controlled by the detailed interface structure and composition and, more specifically, by the characteristics and lifetime of the active catalytic site.

The above discussion demonstrates the central importance of interfaces in solar energy conversion and the critical role that interfaces play in defining the performance of real devices. The motivation for cross-cutting research in the interface science of photo-driven systems reflects this importance. The need for this research is further supported by the major opportunities for scientific advances and the commonality of issues that underlie these diverse technologies. From a theoretical perspective, we are concerned with the relation between charge transport and energy level structure and the physical and chemical nature of the interface. From an experimental perspective, we need tools that are capable of probing buried interfaces in great detail to elucidate the structure, not only of the ideal interface, but also of defects and active catalytic sites. We also need interfacial probes that can follow the evolution of interfaces, not only on the time scale of hours and days, but down to the femtosecond time scale on which the fundamental processes of electronic motion, energy flow, and nuclear displacement in chemical reactions take place. The challenges, both experimental and theoretical, are significant. As we indicate below, however, research advances in the broader scientific community, including

important new experimental and computational approaches, can have a major impact on how we address these vital cross-cutting issues.

Research Issues

Research needs associated with the interface science of photo-driven systems can be divided into the following broad categories: (1) fabrication of controlled interfaces and thin films, (2) development and application of new experimental probes of interface structure and dynamics, and (3) development of new analytical and computational theory capable of elucidating the relationship between interface structure and relevant interface processes, such as excitation, charge separation or recombination, and reaction.

With regard to synthesis of high-quality interfaces, research needs include both the development of highly controlled model research systems and the rational improvement of the array of different interfaces that are currently impacting progress in solar energy conversion. Underlying topics of particular importance include the control of interface composition and structure, both on the atomic- and nano-length scales. The ability to control the nature and density of defects and active catalytic sites is also of crucial importance. A broad study area with major potential for both fundamental science and solar energy conversion is the control of hard-soft interfaces, such as those that arise at the junction between inorganic materials and both conventional organic materials and biological systems. Control of semiconductor heterointerfaces is also crucial to facilitate advances in PV conversion, particularly for high-efficiency multi-junction cells. The control of electrical transport properties at interfaces — a crucial defining factor in preparing high-quality contacts — represents another research need.

Scientists have made great strides in using theoretical techniques to describe the molecular and electronic structures of molecules, solids, and solid surfaces for systems exceeding 1,000 atoms. However, problems related to solar energy conversion impose particular demands on theory. Describing the potential experienced by carriers at material interfaces is an outstanding issue in semiconductor device physics that will be even more important in solar energy conversion because of the central role of interfaces and the variety of interfaces that need to be investigated. The molecular structure and the charge transfer that occurs when molecules or metals are adsorbed on semiconductor electrodes determine the interface potential profile experienced by electrons traversing the interface. By developing an atomic-scale understanding of the relationship between the interface structure and electronic potential, scientists can optimize the properties of interfaces in terms of the carrier transport, carrier separation, and carrier recombination. However, at present, there are no broadly applicable methods for calculating the excited electronic structures of interfaces that could guide the design of electronic properties of interfaces. Moreover, the coupling of molecules to semiconductor continua presents significant challenges for describing the nonadiabatic dynamics leading to charge injection or photocatalytic reactions at semiconductor surfaces. To be able to describe the excited states of extended systems such as regular, as well as more realistic, defective interfaces, we will need to develop new techniques and to extend emerging techniques, such as time-dependent density functional theory.

Carrier generation, relaxation, and transport can be strongly influenced by the properties of bulk and interface materials on the atomic scale. Therefore, we will require techniques that are capable of probing the molecular and electronic structure of materials on an atomic scale at solid-vacuum, solid-liquid, and buried interfaces, as well as for defects in solids. Scanning probe techniques will play a central role in elucidating the atomic structure at solid-vacuum and solid-liquid interfaces. Beyond establishing the molecular structure of interfaces, such techniques will increasingly be used to probe the electronic structure at the atomic level, as well as to determine chemical composition by inelastic tunneling methods. By combining scanning probe and ultra-fast-laser spectroscopic techniques, scientists may be able to probe the fundamental electron dynamics at a single-atom or -molecule level. Laser-based nonlinear spectroscopic techniques will provide vibrational and electronic information about the structure and dynamics at surfaces and buried interfaces that cannot be determined by using scanning probe methods. In particular, techniques such as time-resolved photoemission will provide information about the photo-induced carrier generation, carrier scattering processes that lead to energy relaxation, trapping, and recombination, as well as carrier transport and localization. Techniques that combine high spatial and temporal resolution may be of particular value. New methods, such as Z-scan electron microscopy, will have to be developed for probing atomic-scale buried defects in solids.

Impact

Results from this cross-cutting research have the potential to have a very broad impact on solar energy conversion. The issues, as indicated above, are central to many distinct approaches to solar energy utilization. Significant improvements in the efficiency, reliability, and cost of PV devices can be expected through improved electrical contacts and transparent conductors, as well as through decreased non-radiative processes. Advances in this cross-cutting research direction will also improve the operation and design of dye-sensitized PV devices, and they are critical to the development of photocatalytic approaches to fuel production that exhibit the desired efficiency and selectivity.

THERMAL STORAGE METHODS

Innovative thermal storage methods must be developed to address the need to provide reliable electricity supply based on demand. Demand generally does not coincide with the incident sunlight periods. Achieving this thermal storage capability requires the development of high-energy-density, high-thermal-conductivity, stable, latent heat materials. One promising approach is using encapsulated and nanocrystal polymers.

The operating conditions (i.e., temperature and pressure) of the thermal storage system must match those of the power conversion process and therefore vary from 80–150°C for low-temperature systems to 400–1,000°C for high-temperature systems. Solar-derived fuels are the logical choice for storage at temperatures >1,000°C.

A fundamental understanding of the behavior of phase change storage materials (PCMs) and the relationship between various (sometime undesirable) chemical processes, phase transition, and thermal/chemical stability is crucial for the development of thermal storage methods. The PCMs

must have high latent heat density (>0.3 MJ/kg) and sufficiently high thermal conductivity for enhanced thermal energy charge/discharge processes. Encapsulation of “pockets” of PCM is a possible approach to improve thermal energy transport, while maintaining the chemical and mechanical stability of the material.

Recent developments in nanocrystal polymer composites can be a key to finding a stable cycling solution for thermal storage.

The unique characteristics of solid-solid structural transformations in nanocrystals can lead to a new generation of thermal storage materials. Present materials are limited by the lack of reversibility of structural transformations in extended solids. In contrast, nanocrystals embedded in a “soft matrix” can reversibly undergo structural transitions involving a large volume change per unit cell. This is because a structural transition in a nanocrystal may proceed through a single nucleation event per particle. Further, a nanocrystal can change shape and volume without fracturing or undergoing plastic deformation. Because the barrier to a structural transition depends strongly on the size of the nanocrystals, the hysteresis and kinetics of the structural transition can be controlled. Much of the prior work on structural transitions in nanocrystals has focused on pressure-induced transitions, or transitions that occur at modest temperatures (a few hundred °C), so exploratory work must be performed to find materials and transitions that allow thermal storage under the appropriate conditions for solar energy.

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