PRIORITY RESEARCH DIRECTIONS

REVOLUTIONARY PHOTOVOLTAIC DEVICES: 50% EFFICIENT SOLAR CELLS

To enable solar electricity from photovoltaics to be competitive with, or cheaper than, present fossil fuel electricity costs likely requires devices that operate above the existing performance limit of energy conversion efficiency of 32% calculated for single-junction cells. At present, the best single-junction solar cells have efficiencies of 20–25%. New concepts, structures, and methods of capturing the energy from sunlight without thermalization of carriers are required to break through this barrier and enable solar cells having efficiencies of greater than 50%.

EXECUTIVE SUMMARY

Mature energy conversion technologies typically operate close to their maximum thermodynamic efficiency. For solar energy conversion, this efficiency is between 66% and 87%, depending on the concentration and the spectrum. ***A grand challenge for photovoltaics is the development of high-efficiency, low-cost photovoltaic structures that can reach these ultimate thermodynamic efficiency limits***. Existing photovoltaic devices, which are based primarily on single-junction silicon, have made dramatic improvements over the 50 years of their development, and these solar cells now achieve about three-quarters of the Shockley-Queisser efficiency limit of ~32%. Discovering new technologies, processes, and materials that allow photovoltaic devices to substantially exceed this efficiency while maintaining low cost are critical research goals for photovoltaics.

The viability of achieving these goals has been dramatically increased in the last few years due to the combination of theoretical and material advances, particularly improved understanding of materials and their interaction with growth and defects; and through new approaches, materials, and concepts relying on phenomena allowed by low-dimensional structures. The latter include approaches such as multiple junctions (tandems), optical spectrum shifting, multiple electron/exciton generation, multiple energy level solar cells, and hot carrier solar cells. Substantial scientific challenges exist in each of these approaches, relating to understanding, modeling, and controlling the basic physical mechanisms, as well as to incorporating these physical phenomena into high-performance solar cells (see Figure 20). The development of solar cells based on such principles

Figure 20 A grand challenge of photovoltaics: How to bridge the gap between existing photovoltaic devices and the efficiency limits?

would revolutionize photovoltaics by allowing high-efficiency, cost-effective solar cells, and further, contribute directly to fundamental scientific advances. Moreover, since many solar energy utilization technologies depend on the understanding and control of these physical phenomena, advances in such high-efficiency photovoltaic devices contribute directly toward enhanced understanding that underpins other solar conversion technologies, including organic and photochemical conversion as well as biologically based solar conversion systems.
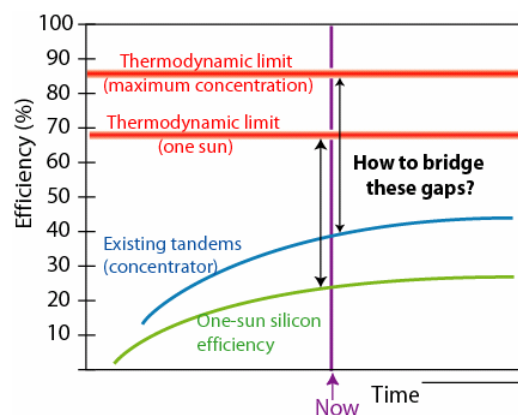
RESEARCH DIRECTIONS

Several paths exist toward the realization of photovoltaic devices with efficiency greater than 50%, including multiple junction solar cells (tandems), solar cells using optical frequency shifting (such as up/down conversion or thermophotonics), multiple exciton generation (MEG) from a single photon, multiple energy level solar cells (such as intermediate band solar cells), and hot carrier solar cells (Marti and Luque 2003; Green 2004). In addition to high efficiency, such cells must also be low in cost, made of polycrystalline thin films grown on inexpensive substrates.

Multiple Junction Solar Cells

Multiple junction solar cells, or tandem solar cells, consist of multiple, single-junction solar cells joined together or stacked upon each other, with each solar cell absorbing the part of the solar spectrum closest to its band gap. Existing tandem devices have achieved efficiencies over 37% (Green et al. 2003) at a concentration of 173 suns, and further efficiency increases can be achieved by increasing the number of different junctions. Despite the high efficiency potential, tandem devices experience a fundamental limitation relating to the availability of materials that simultaneously allow high efficiency through low defect densities and the choice of optimal band gaps. In addition to fundamental advances in understanding defects and recombination, exploring new materials and nanostructures may also revolutionize multiple junction devices by allowing control over band structure, growth, and defects.

Optical Frequency Shifting

Optical frequency shifting cells involve the transformation of the solar spectrum from one with a broad range of energies to one with the same power density but a narrow range of photon energies (see Figure 21). One central feature of these approaches, which include up and down-conversion (Trupke et al. 2002; Trupke et al. 2002a) (i.e., creating a single high-energy photon from two lower-energy photons or creating two lower-energy photons from a single higher-energy photon, respectively) and thermophotonics (Green 2004) (i.e., using the refrigerating action of an ideal light emitting diode to increase the emitted photon energy), is that the transformation of the solar spectrum is done separately with a material that is not part of

Figure 21 Schematic for optical frequency shifting

the actual solar cell, thus increasing the efficiency of an existing solar cell structure via additional coatings or external elements. There are several fundamental challenges in these approaches, including demonstration of cooling due to optical emissions, as well as more efficient processes for up-conversion.
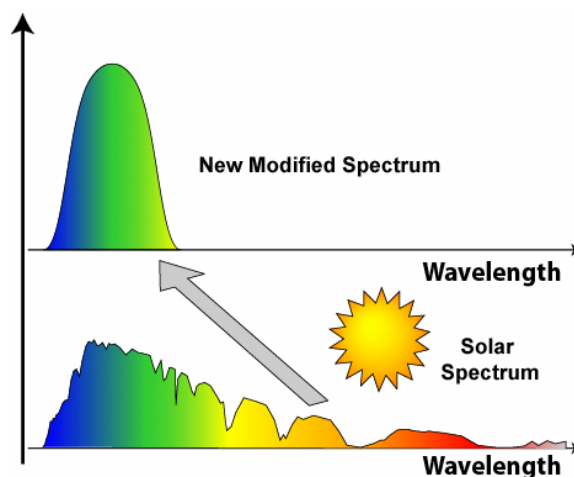
Multiple Exciton Generation Solar Cells

A central limitation of existing solar cell approaches is the one-to-one relationship between an absorbed photon and a generated electron-hole pair. The process of impact ionization, known for decades in bulk semiconductor crystals, allows the conversion of single high-energy photons to multiple electron-hole pairs (Kolodinski et al. 1993), but with relatively low efficiency. Recent experimental reports of multiple exciton generation (MEG) in nano-sized (quantum dot) semiconductors indicate much more efficient generation of multiple electron-hole pairs compared to bulk materials (see Figure 22). For example, semiconductor quantum dots of PbSe and PbS have demonstrated high efficiencies of multiple exciton generation, producing as many as three excitons per absorbed photon (Schaller and Klimov 2004; Ellingson et al. 2005). While the basic physical phenomenon has been demonstrated, additional challenges remain, including efficient transfer and extraction of the generated charges from the nano-structured materials.
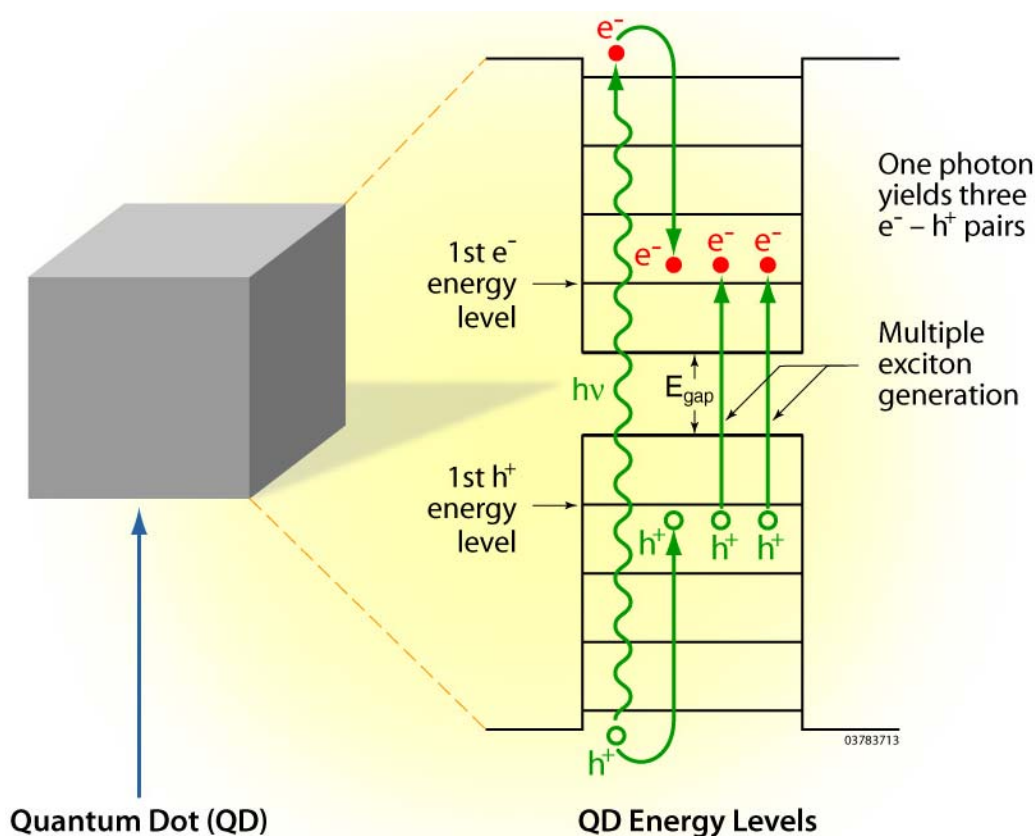
Figure 22 Multiple exciton generation in quantum dots. Because of quantum confinement in the small nanoscale semiconductor QD particle, the energy levels for electrons and holes are discrete. This slows hot exciton cooling and enhances multiple exciton formation. A single absorbed photon that has an energy at least 3 times the energy difference between the first energy levels for electrons and holes in the QD can create 3 excitons. The bandgap of the bulk semiconductor is indicated as E_g.

Multiple Energy Level Solar Cells

In multiple energy level solar cells, the mismatch between the incident energy of the solar spectrum and a single band gap is accommodated by introducing additional energy levels such that photons of different energies can be efficiently absorbed. Multiple energy level solar cells can be implemented either as localized energy levels (first suggested as a quantum well solar cell) or as continuous mini-bands (also called intermediate band for the first solar cell to suggest this approach) (Marti and Luque 2003; Green 2004). Both cases, which are shown in Figure 23, have a fundamental similarity in that the key issue is the generation of multiple light-generated energy levels for electrons.
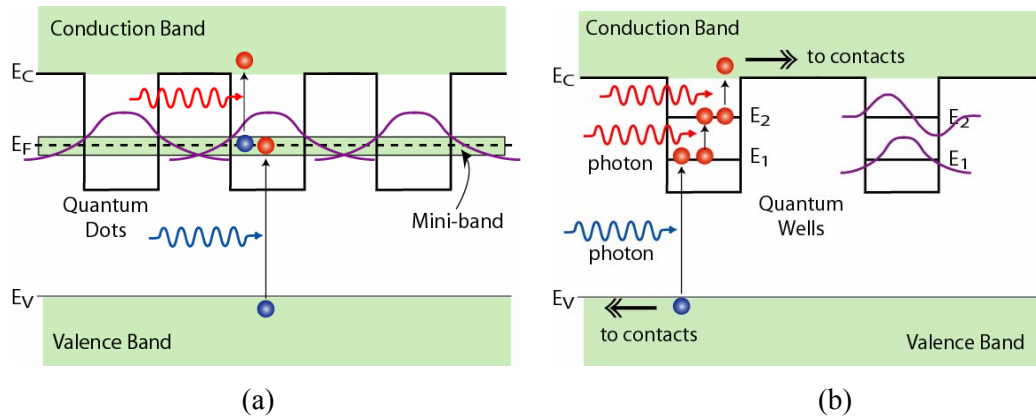

(a)   (b)

Figure 23 (a) Intermediate band solar cell and (b) quantum well solar cell

Hot Carrier Solar Cells

Hot carrier solar cells utilize selective energy contacts to extract light generated hot carriers (electrons and holes) from the semiconductor regions before they have thermalized with the semiconductor lattice (i.e., converted their excess energy to heat) (Ross and Nozik 1982; Würfel 1997). This allows higher efficiency devices (up to a thermodynamic limit of 66% at one sun intensity) by reducing the thermalization (heat) losses in single-junction solar cells. To benefit from this approach, the escape of the hot carriers through the energy-selective contacts must be faster than the various inelastic scattering processes that lead eventually to thermalization to the lattice temperature as shown in Figure 24. Specific materials, in particular, materials with low dimensions such as quantum dots, show slowed carrier cooling and thus hold the promise for realizing such hot carrier solar cells. The obvious prerequisite is reducing the cooling rate well below the hot carrier collection rate and developing the energy-selective contacts for hot carrier collection.
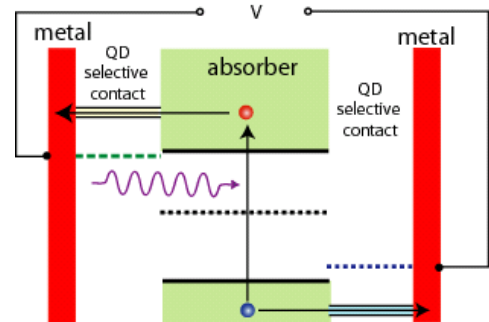

Figure 24 In hot carrier solar cells, carriers are collected before they thermalize.

SCIENTIFIC CHALLENGES

Despite the promise of the new approaches utilizing novel phenomena and materials for energy conversion, substantial scientific challenges exist in understanding and realizing photovoltaic devices that produce >50% efficiency in cost-effective device structures. In addition to the fundamental scientific challenges described above for each new approach, there are additional scientific opportunities that apply to all approaches arising from a deeper understanding of interfaces, non-ideal recombination mechanisms, transport processes, and improved light coupling with the electronic devices.

Control over Interfaces between Dissimilar Materials

Defects within a material or at the interface between two dissimilar materials can cause non-radiative recombination, and, therefore, degrade the performance of solar cells. Defects within a material can originate from a number of causes, including, as examples, those that originate from impurities, or from the defects that can arise from heteroepitaxial growth (Schroder 1997; Aberle 2000).

Interfaces between dissimilar materials also play very important roles in determining the performance of heterostructures. Not only can they affect the crystallographic structure of the thin films on either side of the interface, but they can also be the source of interdiffusion and foreign impurities. As a consequence, interfaces can dominate the transport and recombination of carriers. A fundamental understanding of how to mitigate non-radiative recombination will provide the foundation needed to achieve higher performance for all solar cells. This is especially important for integrated materials because they usually show higher defect densities. There are four general ways to mitigate non-radiative recombination: (a) produce materials with few or no defects, (b) utilize naturally passivated materials (e.g., copper indium diselenide), (c) take advantage of high-quality artificial passivation of materials (e.g., silicon dioxide passivation of silicon), and (d) design materials for the collection of carriers by drift instead of by diffusion.

Interfaces also provide opportunities for harnessing the transmission or reflection of light, or they can be utilized to control the spatial confinement or distribution of photocarriers. For example, thin-film silicon films need light trapping to increase the absorption path, while multijunction structures can benefit by guiding light to the appropriate layer. Careful engineering of the interface shape, composition, and refractive index change can thus improve the properties of a heterostructure, once theoretical and experimental studies have thoroughly characterized the interface of interest.

A fundamental understanding of how to mitigate non-radiative recombination will provide the foundation needed to achieve higher performance for all solar cells, but is especially important for integrated materials because they usually show higher defect densities. Many fundamental materials issues related to the integration of dissimilar materials for harnessing of sunlight are illustrated in Figure 25, including:

Strain Relaxation. Growth of layers on a single- or polycrystalline substrate is affected by the orientation and lattice constant of the crystalline substrate. If two materials (labeled Egap 1 and Egap 2 in Figure 25) are not precisely lattice-matched, strain will increase in the growing layer until relaxation occurs, introducing defects that can propagate throughout the layer. If the relaxation process is understood and can be controlled, then the relaxation can be forced to occur within a confined part of the device, allowing the layers of interest to remain pristine. Experimental and theoretical studies may determine the growth parameters (growth temperature, growth rate, rate of change of lattice constant, etc.) that are key to controlling the relaxation and how they are affected by the composition of the epilayers. Ultimately, the goal of these studies would be to define the limits of the composition range that can be accessed with near-perfect crystal quality while minimizing the thickness of the graded layer and final strain (wafer bow) of the sample.

Templating. Methods are needed to enable flexible control of the crystallographic structure and morphology of active semiconductor absorber layers that are dissimilar from the underlying support substrate. Synthesis and processing methods that enable template layers to control crystal structure, phase, and in-plane and out-of-plane orientation of thin films synthesized on inexpensive substrates are desirable. Such methods include vapor-deposited template films with controlled microstructures, transferred single crystalline layers, lithographically stamped patterns, and colloidally assembled materials, among others.

Light-trapping Structures. Increasing the coupling between the incident radiation and the absorber material is a central component of high-efficiency solar cells. Historically, this has been done by using simple macroscale design principles, such as minimizing the front surface reflectivity of a solar cell. Recently, tremendous advances have been made in the understanding of periodic and non-periodic optical cavity and waveguide structures (e.g., photonic crystals, plasmonic materials that control optical dispersion). Finding methods for incorporating these types of structures and materials onto inexpensive substrates, and integrating them with multilayer heterostructures, constitutes a very significant challenge for fundamental materials science and engineering.
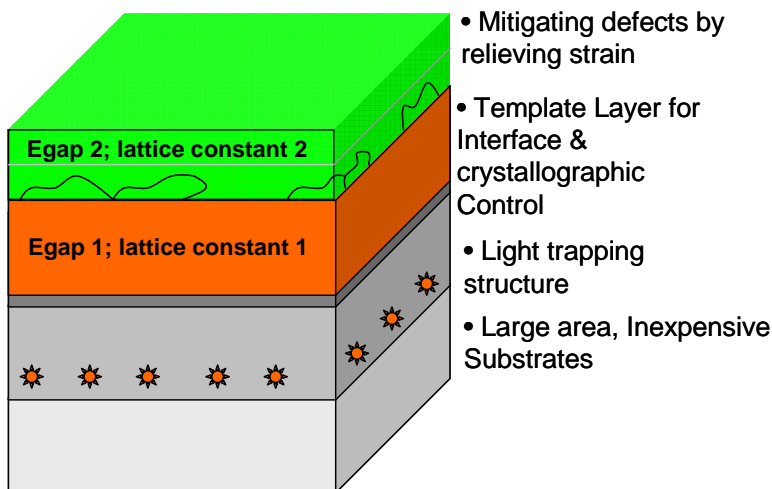

Figure 25 Integration of dissimilar materials to harness sunlight

Control over Nucleation and Growth for Producing High-quality Thin Films

The growth of a thin semiconductor layer on an inexpensive substrate usually results in a polycrystalline material. The properties of polycrystalline materials are challenging to study because each individual grain is likely to have a different size, orientation, shape, surface termination, structural quality, and impurity content. A variation in any of these attributes can translate into variations in device performance, and thus an associated reduction in manufacturing yield.

The challenge of characterizing, modeling, and controlling polycrystalline film properties is formidable. Figure 26 illustrates how control over the nucleation and growth can yield control over grain size, orientation, and shape, and, therefore, material quality. The remarkable advances in nanostructure synthesis over the past decade provide scientists with tremendous opportunities for controlling the structure of thin polycrystalline films. Similar advances in materials characterization tools provide new opportunities for quantifying and thus eventually controlling grain boundaries, defect states, etc. Understanding and controlling thin-film nucleation and growth are key for both achieving high-performance photovoltaics and for achieving practical success in the manufacturing environment.
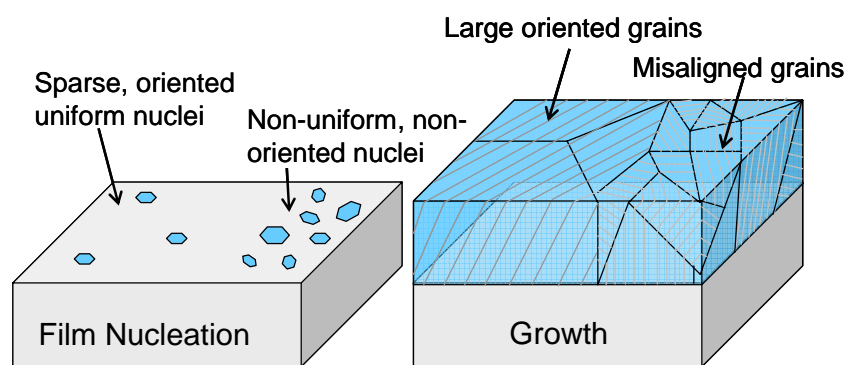

Figure 26 Controlling nucleation and growth

Improve Understanding of Carrier Dynamics at Interfaces

Interfaces between different materials are necessary ingredients of every type of solar cell. Their number increases with the number of different materials and with the complexity of the solar cell structure. Electronic interface states can fall within the band gap but show up also as resonances isoenergetic with the electronic bulk states. Recent advances in experimental and theoretical techniques now give access to real-time measurements and modeling of the underlying interfacial charge carrier dynamics on the relevant time scales. The latter range from a few femtoseconds to milliseconds. The actual energy distribution of hot charge carriers in semiconductors under solar irradiation with up to a thousand-fold concentration can remain non-thermalized and thus cannot be characterized by the lattice temperature. A realistic description of interfacial loss processes requires (a) a model for the respective charge carrier dynamics that is based on the detailed atomic and electronic structure of bulk interface and (b) a sufficiently detailed time-dependent model calculation that comprises all the relevant electronic levels and all

the relevant elastic and inelastic scattering processes that are specific for the respective materials and their interfaces. It has been found that energy relaxation of hot carriers is delayed when the latter are transiently captured in empty surface states and that there are direct optical transitions occurring between empty and occupied interface states. There are specific interfacial recombination processes involving hot, thermalized, and trapped charge carriers. Reaching the best conversion efficiencies will require a deeper understanding of the carrier dynamics and losses that occur at interfaces, and control over the best atomic design of such interfaces.

Non-ideal Recombination Mechanisms

Recombination mechanisms that compete with the separation and collection of electrons and holes are a critical controlling factor in photovoltaic energy conversion. However, despite their importance, multiple fundamental unknowns exist, even for existing materials and devices, such as how defects interact with materials and growth conditions to control mobility and minority carrier lifetime. The determination of the many different types of recombination mechanisms is even more difficult in many of the new approaches, in which not only understanding but also measurement and characterization of the recombination mechanisms represents a significant challenge.

Transport Properties of Hot and Thermalized Carriers in Materials of Different Dimensions and Different Time Scales

It is well established now that moving from bulk macroscopic semiconductor materials to reduced dimensions (quantum dots, wires, and wells) leads not only to a stronger influence of the interface due to its enhanced area compared to the bulk phase but in addition to drastic qualitative changes in bulk properties. A particularly interesting aspect concerns the reduction in the rate of inelastic scattering processes for hot carriers (thermalization) in semiconductors of reduced dimensions. A prolonged lifetime for excited electronic states, sometimes referred to as *slowed-down cooling*, holds the promise of realizing hot carrier solar cells where the hot carriers are extracted via energy selective contacts (Green 2004; Würfel 1997; Nozik 2001).

The recently shown enhanced probability for generating multiple excitons from one absorbed photon in certain semiconductor quantum dots underscores the need for extensive research in the direction of surpassing the one band gap conversion limit with solar cell concepts based on semiconductor structures of reduced dimensionality (Schaller and Klimov 2004; Ellingson et al. 2005; Nozik 2002).

Enhanced Coupling of Solar Radiation to Absorber Materials

Increasing the coupling between the incident radiation and the absorber material is a central component of high efficiency solar cells. Historically, this has been done by using simple macro-scale design principles, such as minimizing the front surface reflectivity of a solar cell. Recently, tremendous advances have been made in understanding of periodic and nonperiodic optical cavity and waveguide structures (e.g., photonic crystals, plasmonic materials) that control optical

dispersion. These structures can control the rate of spontaneous emission and absorption via interaction of the local density of optical modes with dipole absorptions and emitters. For solar absorbers that employ heterogeneous assemblies of nanostructures or optical wavelength-scale structures, coupling of incident radiation to the solar absorber can be enhanced by use of periodic dielectric or metallodielectric structures that modify or control the density of optical modes available for light absorption and light emission.

POTENTIAL IMPACT

The majority of existing terrestrial photovoltaic devices (>99%) are based on single-junction photovoltaic concepts which have an efficiency limit of ~32%. A new generation of photovoltaic devices can allow both dramatic improvements in efficiency and lower cost. However, the realization of such devices faces multiple scientific challenges. Solutions to these scientific challenges will not only allow solar energy to tunnel through the cost/performance barriers faced by existing photovoltaic devices, but will also contribute to the issues faced by many of the solar conversion technologies, such as organic, photochemical, thermophotovoltaic, and biologically inspired energy conversion systems. The potential impact of being able to put any material on any other material while still maintaining excellent performance will revolutionize the photovoltaics industry by allowing the integration of multiple materials into multijunction cells, enabling achievement of 50% efficiency and associated growth of a multijunction concentrator industry. Furthermore, this capability will allow high-performance, thin silicon cells to overcome the current shortage of silicon feedstock.

REFERENCES

A.G. Aberle, "Surface Passivation of Crystalline Silicon Solar Cells: A Review," *Progress in Photovoltaics* **8**, 473 (2000).

R.J. Ellingson, M.C. Beard, J.C. Johnson, P. Yu, O.I. Micic, A.J. Nozik, A. Shabaev, and A.L. Efros, "Highly Efficient Multiple Exciton Generation in Colloidal PbSe and PbS Quantum Dots," *Nano Lett.* **5**, 865 (2005).

M. Green, *Third Generation Photovoltaics: Advanced Solar Energy Conversion*. Springer: Berlin, Germany (2004).

M.A. Green, K. Emery, D.L. King, S. Igari, and W. Warta, "Solar Cell Efficiency Tables (version 23)," in *Progress in Photovoltaics*, **13**, 55 (2003).

S. Kolodinski, J.H. Werner, T. Wittchen, and H.J. Queisser, "Quantum Efficiencies Exceeding Unity due to Impact Ionization in Silicon Solar Cells," *Appl. Phys. Lett.* **63**, 2405 (1993).

A. Marti and A. Luque, *Next Generation Photovoltaics: High Efficiency through Full Spectrum Utilization*. Institute of Physics: Bristol, U.K. (2003).

A.J. Nozik, "Spectroscopy and Hot Electron Relaxation Dynamics in Semiconductor Quantum Wells and Quantum Dots," *Annu. Rev. Phys. Chem.* **52**, 193 (2001).

A.J. Nozik, "Quantum Dot Solar Cells," *Physica E* **14**, 115 (2002).

R.T. Ross and A.J. Nozik, "Efficiency of Hot-Carrier Solar Energy Converters," *J. Appl. Phys.* **53**, 3813 (1982).

R. Schaller and V. Klimov, "High Efficiency Carrier Multiplication in PbSe Nanocrystals: Implications for Solar Energy Conversion," *Phys. Rev. Lett.* **92**, 186601 (2004).

D.K. Schroder, "Carrier Lifetimes in Silicon," *IEEE Transactions on Electron Devices* **44**, 160 (1997).

T. Trupke, M.A. Green, and P. Würfel, "Improving Solar Cell Efficiencies by Up-conversion of Sub-band-gap Light," *J. Appl. Phys.* **92**, 4117 (2002).

T. Trupke, M.A. Green, and P. Würfel, "Improving Solar Cell Efficiencies by Down-conversion of High-energy Photons," *J. Appl. Phys.* **92**, 1668 (2002a).

P. Würfel, "Solar Energy Conversion with Hot Electrons from Impact Ionization," *Sol. Energy Mater. Sol. Cells* **46**, 43 (1997).

MAXIMUM ENERGY FROM SOLAR PHOTONS AT LOW COST: DESIGNED PLASTIC PHOTOVOLTAIC STRUCTURES

"Plastic" solar cells made from molecular, polymeric, or nanoparticle-based structures could provide flexible, inexpensive, conformal, low-cost solar electricity systems. At present, the efficiencies of such systems are too low (<5%, generally 2% or less) to be useful; performance needs to be improved by a factor of 5–10. New materials chemistry, new device designs, and fundamental understanding of the factors that limit the performance of these systems are needed.

EXECUTIVE SUMMARY

Organic photovoltaic (OPV) devices are in a comparatively early stage of development. Since the early proof-of-principle work on organic photovoltaics in the mid-1980s, total solar to electrical energy conversion efficiencies have been pushed to *ca.* 5%. A vigorous period of research and development is needed to refine structures, processing, and cell fabrication techniques to increase the efficiency of OPVs five- to ten-fold with respect to current values.

Since the early developments in this field, substantial improvements have occurred in synthesis methods for fabrication of the molecular, polymeric, and nanocrystalline building blocks used to make organic photovoltaic converters. Significant advances also have been made in the techniques used to characterize organic systems and the fundamental processes involved in operation of organic photovoltaics (e.g., scanning probe microscopy, time-resolved optical methods, etc.). The development of high-efficiency organic solar

Figure 27 Construction of a typical organic photovoltaic device. The active layer (red) can be a bilayer of vapor-deposited molecules, or a bulk heterojunction containing a polymer and C_{60} or an inorganic quantum structure.

cells could lead to a revolution in solar electrical power generation — the promise of an inexpensive "solar paint" that could be deployed over large areas in a convenient and conformable format.

The research agenda to achieve these goals requires the design and development of robust molecular systems with structural, optical, and electronic properties optimized for photovoltaic energy conversion. This activity will necessarily include a close coupling of molecular and device theory, directed organic synthesis and purification, photophysical characterization, and processing. Organic solar cells that are based on the photogeneration of excitons (bound electron-hole pairs) or excited states, rather than the direct formation of charge carriers, necessitate a detailed understanding of the fundamental process of charge separation and recombination at nanostructured interfaces between organic and hybrid interfaces. Parallel research efforts will involve design of cell architectures to optimize the interactions of light with
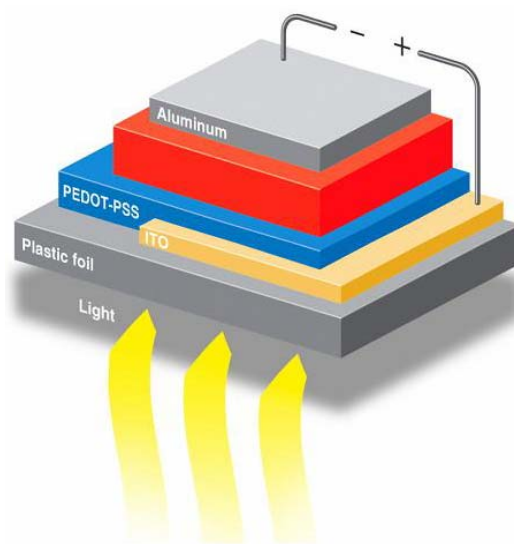
these new organic structures, and to maximize energy extraction efficiencies. The research will strive to achieve new, low-cost, scalable fabrication methods.

RESEARCH DIRECTIONS

Organic Photovoltaic Structures

The current state of the art in solar to electrical conversion efficiency attained with OPV cells is in the range of 3–5% (Padinger et al. 2003; Peumans and Forrest 2001; Wienk et al. 2003; Brabec 2004) (see Figures 27 and 28). To achieve the breakthroughs that will bring OPV cell technology to the point where it is competitive with other renewable power sources, new molecular, polymeric, and inorganic semiconductor quantum-confined structures for photovoltaic applications are needed.

The most efficient polymer-based photovoltaic cells fabricated to date (Wienk et al. 2003; Brabec 2004) consist of bulk heterojunction structures containing poly(phenylene vinylene)s (PPVs) or poly(alkylthiophene)s (PATs) blended with soluble C_{60} derivatives, such as PCBM (Figure 29). While these systems clearly have merit in that there is a body of synthetic chemistry to guide the synthesis and purification of PPVs, PATs, and C_{60} derivatives, new families of strongly light-absorbing, electron donor- and acceptor-type polymers are needed for photovoltaic applications. Key elements that must be addressed in the development of new organics include broad, tunable absorption throughout the 400–1300 nm spectral region, the ability to control highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels, and high hole and electron carrier mobilities. A number of donor-type polymers with good hole mobility are already available; however, there is a need for development of new acceptor-type structures that feature high electron mobility. Synthesis of block, graft, or star polymers featuring variable HOMO-LUMO gap donor and acceptor segments should be pursued, as well as dendrimer structures. Polymers that are functionalized to facilitate processing—for example, to tune surface
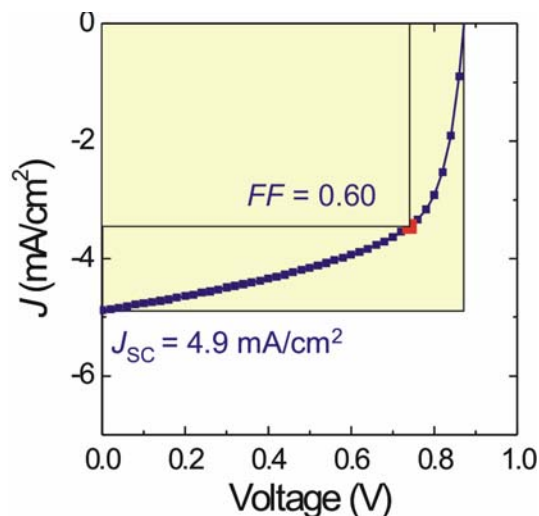
Figure 28 Current-voltage curves of a good bulk heterojunction device: Short circuit current, $J_{SC} = 4.9$ mA/cm^2; open circuit voltage, $V_{OC} = 0.84$ V; and fill factor, FF = 60%
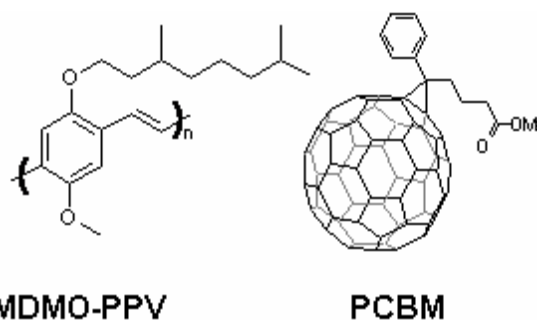
Figure 29 A typical conjugated polymer (MDMO-PPV) and a soluble derivative of C_{60} (PCBM) used in a bulk heterojunction device

wettability or post-deposition cross-linking, or to allow layer-by-layer deposition—are also key objectives.

Considerable success has also been achieved with molecule-based OPV systems that are deposited onto conducting substrates, predominantly by vapor deposition and in some cases by wet deposition methods. Deposition methods have been developed to produce nanostructures or liquid crystalline phases that enhance exciton dissociation and carrier mobility. Although advances have been made in the development of molecules for OPVs, there is a strong need for new compounds. The guiding principles behind the development of new small-molecule systems are similar to those for the polymers (i.e., molecular systems that afford tunable optical absorption through the 400–1,300 nm range, control of redox levels, and high exciton, hole, and electron mobility). General synthetic strategies leading to molecular structures that deposit into ordered phases with strong, long-range inter-chromophore interactions, such as J- or H-aggregates, are desired.

A third approach that has shown some measure of success involves "hybrid" photovoltaic structures consisting of blends or composites of organic polymers and inorganic semiconductors (Huynh et al. 1999; Sun et al. 2005). Success here has been attained primarily by using donor-type conjugated polymers (PPVs or PATs) as composites with nanocrystalline inorganic semiconductors (e.g., metal oxides, CdS, CdSe, and CdTe). In these systems the semiconductors can enhance the visible and near-infrared absorption and also serve as acceptors with good electron mobility. Continued work in this area is needed. Inorganic semiconductors have a clear advantage in providing strong near-infrared absorption; they may also provide a significant boost in carrier generation efficiency due to photon down-conversion processes. Carrier mobility can be enhanced by controlling the dimensionality of the inorganic semiconductors and the packing of the organic molecules. The interface between the organic and inorganic phases can be controlled by using chemical methods to control the functionality of the semiconductor surface.

The reason for the large drop in energy between that of the absorbed photon and the resulting open-circuit voltage (V_{oc}) is not understood. Extensive theoretical and experimental work is needed to increase the power conversion efficiency of such photovoltaic devices by an order of magnitude. The open-circuit voltage is related to the offset between the HOMO level of the electron donor/hole transport phase and the LUMO level of the electron acceptor/transport phase, although the exact mathematical relationship is not fully developed. The origin of the large difference between V_{oc} and the HOMO-LUMO band offset must be understood, as should the role of the difference in work functions of the contact electrodes (see Figure 30).

Exciton and Carrier Transport

Photoexcitations in organic semiconductors are fundamentally different from those in inorganic semiconductors. Whereas light absorption in inorganic semiconductors leads to the direct generation of mobile charged carriers, light absorption in organic semiconductors leads to the generation of excitons that typically have an associated binding energy in excess of 0.2 eV. Exciton and charged carrier transport in organic semiconductors is at the heart of the operation of these devices; their optimization will require a detailed microscopic understanding of the
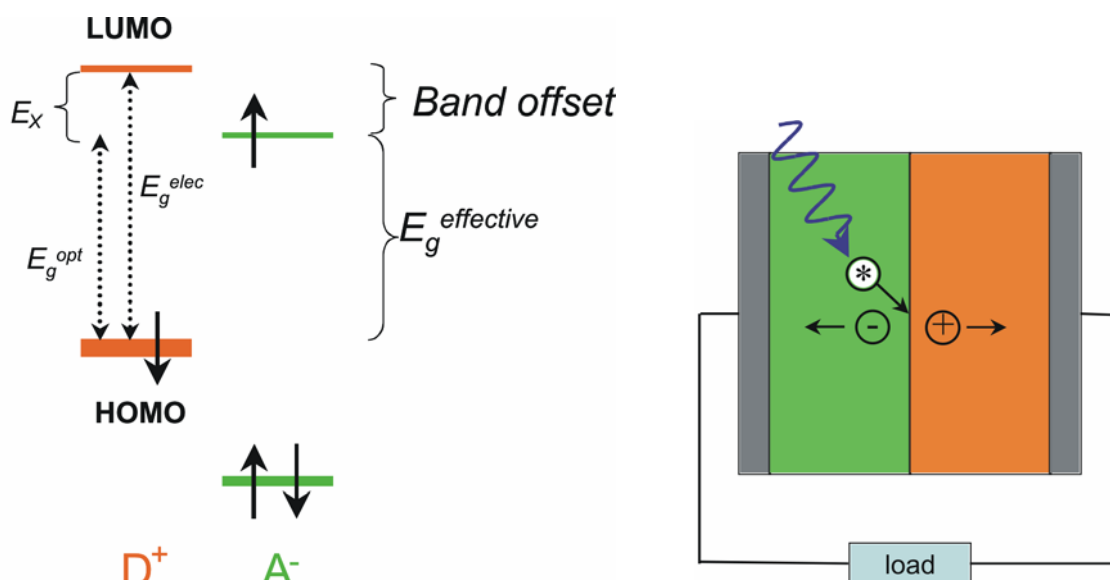
Figure 30 Schematic diagram (right) of an excitonic solar cell comprising a donor (orange) and an acceptor (green) species. An energy-level diagram (left) with excitation into the donor shows the optical and electronic bandgaps of the donor and acceptor and the band offset relative to the exciton binding energy (E_X).

transport mechanisms, which take a variety of different forms, depending on the quasi-particle that is being transported. Excitons are charge-neutral and are transported by diffusion, while charged carriers are transported by diffusion and/or drift in the built-in electric fields resulting from the electrical contacts. The degree of structural order of the material is important in determining transport properties. In the disordered limit (which includes most polymers), carrier transport occurs predominantly via hopping between spatially localized states, the energy distribution of which determines the intrinsic mobility. In the ordered limit of single crystals, weak scattering among delocalized states produces band-like transport. Strong charge lattice interactions lead to polaron states, which exist in both disordered and ordered structures. Understanding the role of deep energy traps in highly disordered materials is vital for controlling both charge transport and exciton lifetimes. These traps must be identified and characterized individually in crystalline samples; this knowledge can be used for optimization of the extrinsic mobility in device structures. A key component of this work is close interaction between mobility measurements, transport spectroscopies, and theory, including electronic structure and transport theories.

Charge Separation and Recombination at the Interface between Nanostructures

Although singlet excitons are the predominant photogenerated species, intersystem crossing to the triplet state yields species that are longer-lived and lower in energy. Their role in enhancing light-emitting devices has been a key success story, but little is known about their impact in organic photovoltaics. Whether they are essential or must be avoided at all costs are questions that need addressing. Although the exciton dissociation process is of fundamental importance to extracting energy from absorbed photons in OPV structures, it is also essential to inhibit the

process of charge carrier recombination. Transport of the resulting charged carriers away from the interface so as not to form bound interface states is an equally important process to control, but both these processes are poorly understood. The role of interfacial energy off-sets, dipole layers, exciton binding energy, and spin states must be understood, and their relationships to the electronic structure of the interface are important issues to address.

Semiconductor quantum dots, metal nanoparticles, and carbon nanotubes are all examples of species that can be incorporated in an organic host to promote exciton dissociation and/or additional charge carrier generation and transport. Similarly, photoexcited semiconductor nanoparticles can undergo charge transfer upon contact with metal nanoclusters (such as gold and silver). Such charge redistribution can influence the energetics of the composite by shifting the Fermi level. A better understanding of the mediating role of metal nanoclusters, including their size and shape dependence on the storage and transport of electrons, is needed to design the next generation of hybrid systems. Metal nanoparticles have potential as components of the interconnecting junction in a tandem solar cell, where they act as recombination centers, but they can also dramatically influence the optical properties of the surrounding medium.

Third-generation OPV

To achieve a device with efficiency that approaches 50% will require the development of organic species and device architectures that can extract more energy from the solar spectrum than can a single-junction device. The two basic methods for achieving this goal are the development of efficient structures for up- and down-conversion of solar photons to match an existing, single-junction device; or the construction of multiple, stacked single-junction devices that are optimized for specific wavelengths of light within the solar spectrum (Figure 31).

To achieve these objectives, research into the relationship between the excited-state properties of organic molecules and their structure is needed. For photons absorbed above the optical bandgap, such a strategy can lead to systems with the ability to either down-convert the initial excited excitons into multiple ground-state excitons and ultimately into multiple charge carriers, or systems that can facilitate the up-conversion of sub-optical bandgap solar photons into excitons.

The progress made in the direction of stacked (tandem) solar cells will be facilitated by the development of new deposition procedures that can be adapted to provide the required structures. Such issues as layer thickness and the creation of multiple interfaces are nontrivial aspects of the problem that are far from optimized and require attention. Furthermore, the need for materials that can act as interconnectors for balanced
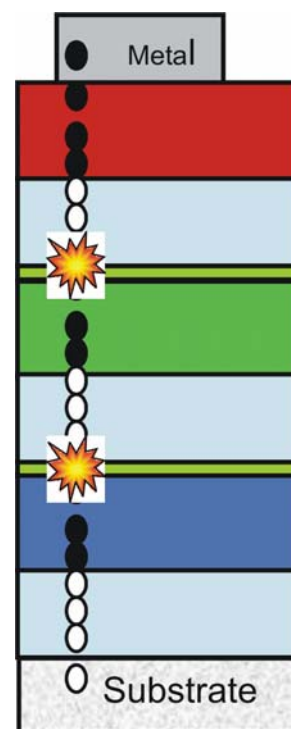
Figure 31 Schematic of a multi-layered, tandem organic solar cell with three stacked solar cells designed to absorb different solar photons that enter through the substrate. Balanced charge transport in each cell is indicated with efficient recombination at the two interconnectors.

carrier injection between the individual cells has received little attention. Use of colloidal metals to fulfill this function has proven to be surprisingly successful; the amount of metal required is minimal, and beneficial field-enhancement effects improve the absorption properties of the surrounding medium. Although the basic effects are understood, significant improvements in device performance depend upon a far more detailed understanding of the properties of these and related species when they are embedded in organic structures.

The contact electrodes continue to play a significant role in controlling device performance. The deposition of metals as one contact and the use of ITO as the transparent conducting electrode are limiting factors. New strategies are needed to develop transparent conductors and substrates that take into account their "end use" in organic-based solar energy conversion devices. This problem can be addressed by focusing on the interface with the existing transparent oxides or by developing new molecule-based conductors that provide better compatibility.

SCIENTIFIC CHALLENGES

Key scientific challenges that must be overcome include optimizing the target molecular, polymeric, and nanocrystalline structures to produce systems that will provide extraction of energy over the full range of the solar spectrum, including the challenging near-infrared region. There is also a need to understand the relationship between electronic structure and excited state properties of the constituent species of these new systems and to understand how this relationship is affected through their interactions with each other. The development and understanding of structures that can exhibit efficient frequency up-conversion and down-conversion for advanced, third-generation device structures will also benefit from such a fundamental understanding. Factors that control the processes that occur at the interfaces between dissimilar phases pose an additional challenge that must also be addressed. This includes the interface within the components of the active photoconversion medium, at the interface between stacked junctions of a tandem design and at the interface with the external contacts. The challenge is to understand how to manipulate and enhance the transport of excitons to the interface, where they can be dissociated and the resulting charge carriers transported away, while inhibiting any recombination processes.

POTENTIAL IMPACT

The potential impact of success in the development of new organic photovoltaic systems and device structures will be high-performance, light-weight, conformable, photovoltaic solar arrays that contain sustainable and nontoxic species.

REFERENCES

C.J. Brabec, "Organic Photovoltaics: Technology and Market," *Sol. Energy Mater. Sol. Cells* **83**, 273–292 (2004).

W.U. Huynh, X. Peng, and P. Alivisatos, "CdSe Nanocrystal Rods/Poly(3-hexylthiophene) Composite Photovoltaic Devices," *Adv. Mater.* **11**, 923–927 (1999).

F. Padinger, R.S. Rittberger, and N.S. Sariciftci, "Effects of Postproduction Treatment on Plastic Solar Cells," *Advanced Functional Materials* **13**, 18 (2003).

P. Peumans and S.R. Forrest, "Very-high-efficiency Double Heterostructure Copper Phthalocyanine/C_{60} Photovoltaic Cells," *Appl. Phys. Lett.* **79**, 126–128 (2001).

B.Q. Sun, H.J. Snaith, A.S. Dhoot, S. Westenoff, and N.C. Greenham, "Vertically Segregated Hybrid Blends for Photovoltaic Devices with Improved Efficiency," *J. Appl. Phys.* **97** (2005).

M.M. Wienk et al., "Efficient Methano[70]fullerene/MDMO-PPV Bulk Heterojunction Photovoltaic Cells," *Angew. Chem.*, *Int. Ed.* **42**, 3371–3375 (2003).

NANOSTRUCTURES FOR SOLAR ENERGY CONVERSION: LOW COST AND HIGH EFFICIENCIES

Conventional solar cells require relatively pure absorbers to produce electrical current, whereas nanostructured absorbers can circumvent this limitation by enabling collection of carriers in a direction orthogonal to that of the incident light. Such systems have produced test devices having up to 10% efficiency, but typical devices yield 3–5% efficiencies over large areas and have long-term stability issues. New absorber combinations, control over the nanostructure of such systems, and a fundamental understanding of the operating principles of such devices are needed to enable a new generation of systems having two- to five-fold improvement in efficiency, low cost, and long-term stability.

EXECUTIVE SUMMARY

Although conventional solar cells based on silicon are produced from abundant raw materials, the high-temperature fabrication routes to single-crystal and polycrystalline silicon are very energy intensive and expensive. The search for alternative solar cells has therefore focused on thin films composed of amorphous silicon and on compound semiconductor heterojunction cells based on semiconductors (e.g., cadmium telluride and copper indium diselenide) that can be prepared by less energy-intensive and expensive routes. A key problem in optimizing the cost/efficiency ratio of such devices is that relatively pure materials are needed to ensure that the photo-excited carriers are efficiently collected in conventional planar solar cell device designs. The use of nanostructures offers an opportunity to circumvent this key limitation and therefore introduce a paradigm shift in the fabrication and design of solar energy conversion devices to produce either electricity or fuels.

The absorber thickness is dictated by the absorption properties of the semiconductor being used; for example, 100 μm of Si or 1–3 μm of GaAs are required to absorb fully incident sunlight, so that incident photons are not wasted by virtue of being transmitted through the entire device assembly. In turn, the absorber must be sufficiently pure that the excited states produced by light absorption can survive for the required time and distance to be collected in an external circuit and do not instead recombine to produce heat. The required absorption length therefore dictates the minimum purity and cost needed to achieve the required carrier collection lengths. The use of nanostructured and possibly nanoporous systems, however, offers an opportunity to satisfy these two constraints, by collecting carriers in a direction that is orthogonal (nominally perpendicular) to the one in which light is absorbed, as illustrated in Figure 32. In this way, such an approach offers the potential for obtaining high energy conversion efficiency from relatively impure, and therefore relatively inexpensive, photoconverters.

One important example of such a structure is provided by mesoscopic dye-sensitized solar cells, which generally involve use of a highly porous film of randomly ordered nanoparticles of a transparent nanocrystalline oxide, such as TiO_2, coated with an ultrathin layer of light absorber (e.g., dye molecules or semiconductor quantum dots). When photo-excited, the absorber injects electrons into the oxide nanoparticles and creates a positive charge in the absorber. After electron injection, the positive charge is neutralized by electron transfer to the oxidized dye from a liquid
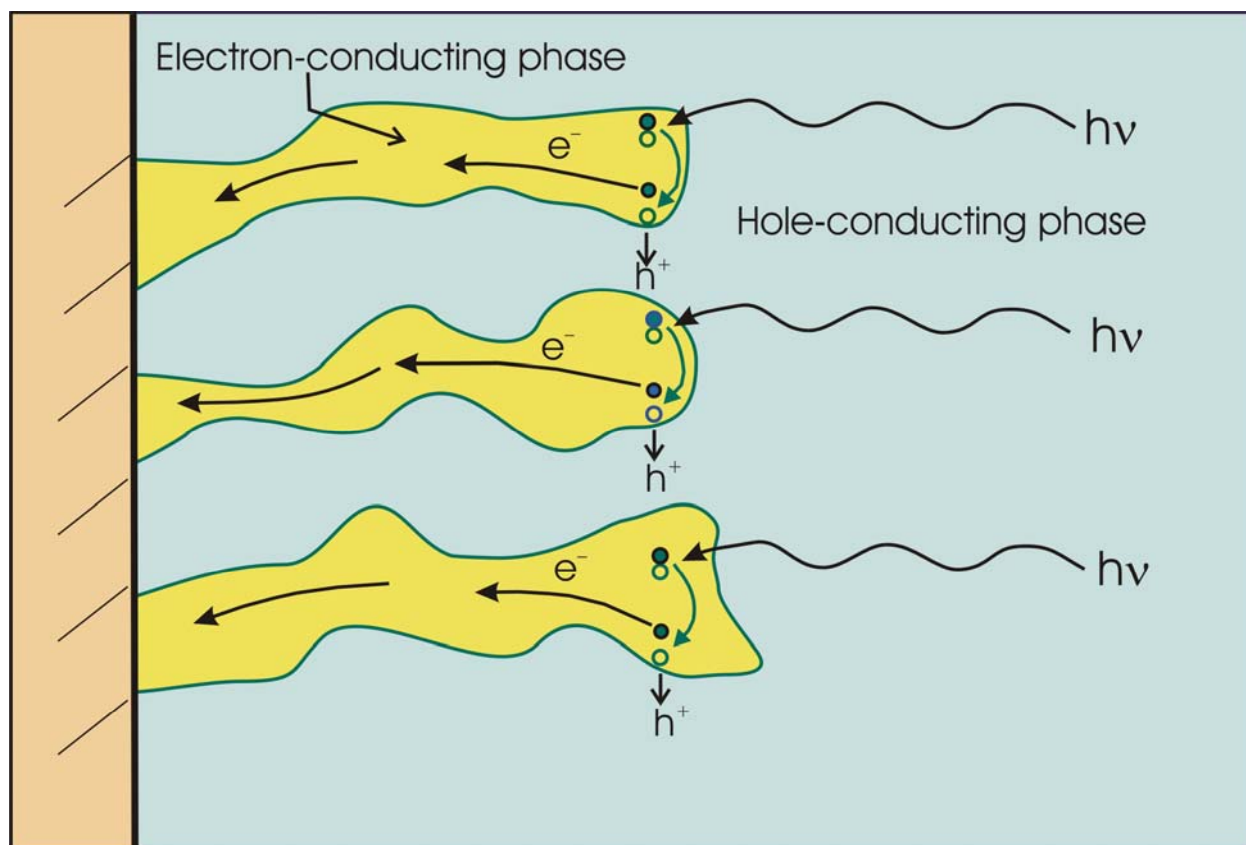
Figure 32 One important example of such a structure is provided by mesoscopic dye-sensitized solar cells (Grätzel 2000; Grätzel 2001), which generally involve use of a highly porous film of randomly ordered nanoparticles of a transparent nanocrystalline oxide, such as TiO_2, coated with an ultra-thin layer of light absorber (e.g., dye molecules or semiconductor quantum dots).

or solid medium that permeates the porous structure; this regenerates the absorber and completes the cycle. Another example of such nanostructured devices is the use of semiconductor nanowires or nanorods to absorb light and transfer the charge carriers over a very short distance to the collecting phase, which can be a conducting polymer, an electrolyte (a liquid charge conductor), or an inorganic conductor. Yet another example is an interpenetrating network of n-type and p-type organic semiconductors that form heterojunction-type solar cells.

An exciting aspect of this approach is that the generic concept of the nanostructured cell can be extended to a range of novel configurations involving different light absorbers and electron-hole conducting phases. A key property of the thin nanostructured film is that since charge carrier pairs are generated only near the interfaces and are separated rapidly into two different phases, bulk recombination and semiconductor instability are avoided. Junction recombination does, however, have to be minimized, and the surfaces of such systems need to be controlled to ensure that they have a relatively low level of defect-driven electrical recombination sites, to allow carriers to actually be collected from such devices. Fabrication of these types of cells can be remarkably simple, and efficiencies over 11% have already been reported for some dye-sensitized nanostructured systems. There is considerable potential for increasing this performance to 20% by imaginative approaches that exploit the rapidly growing field of

nanoscience. This efficiency objective provides a strong motivation for a program of basic research that aims to understand and control all the factors that determine cell performance in nanostructured systems. Building this knowledge base will provide the platform from which to launch an effort to achieve efficiencies beyond the Shockley-Queisser limit by incorporation of approaches such as multijunction cells and photon up-conversion.

RESEARCH DIRECTIONS

Multiple Charge Carrier Generation

Calculated thermodynamic efficiency limits in single-junction solar cells (~32%) assume that absorption of an individual photon results in the formation of a single electron-hole pair and that all photon energy in excess of the energy gap is lost as heat. This limit, however, can be surpassed via multiple exciton (electron-hole pair) generation (MEG) by single-photon absorption as was predicted (Nozik 2001; Nozik 2002) and observed optically in PbSe and PbS quantum dots (Schaller and Klimov 2004; Ellingson et al. 2005). The ability to generate multiple charge carriers upon absorption of one photon could lead to greatly enhanced photocurrent and, ultimately, to very high efficiency solar cells.

Exploit the Unique Properties of Nanostructured Systems to Develop New Cells with Solar Efficiencies of 20%

Current mesoporous nanocrystalline films used in dye-sensitized solar cells consist of a random nanoparticle network and a disordered pore structure. Such films are characterized by slow electron transport. Moreover, because of the wide particle distribution and disordered nature of the pores, not all of the internal surface area of a film is accessible to the sensitizer. Also, it is difficult to fill the pores completely with viscous, quasi-solid, or solid ionically or electronic conductors, which serve to transfer photogenerated holes away from the sensitizers following charge separation. Development of ordered nanostructured, inorganic electrodes could lead to more effective incorporation of ionically or electronically conducting materials (ionic gels, polymers, etc.) within the pore structure and potentially to faster charge transport. Also, more uniformly sized particles coupled with periodic order could facilitate films favoring preferred crystal faces for optimizing charge separation. Developing new stable, near-infrared absorbing molecular and quantum confined sensitizers with increased red absorbance would allow for thinner TiO_2 layers, which would result in lower charge recombination and higher overall efficiency. Confining photons to a high-refractive-index sensitized nanostructured oxide film is another approach to enhance the red response of the cells. For instance, a two-layer structure consisting of submicron spheres and a nanoparticulate TiO_2 layer has been used to enhance light collection owing to multiple scattering. Incorporation of more advanced light management strategies, such as photonic band gaps, also offers promise for enhancing the red response of the cell.

Also, relatively unexplored are self-assembling molecular, supermolecular, and inorganic interface layers having, for example, a broad spectral response and/or the electronic capability of directing the resulting energy vectorially as excitons or charges toward the nanostructure

interface for charge separation. For instance, a self-assembling, thin inorganic charge-mediating layer with appropriate electronic levels, covering the nanostructured surface, could allow for vectorial charge transfer from the sensitizer to the conduction band of the semiconducting oxide, while blocking the back electron transfer to the oxidized sensitizer or to the hole-carrying species in the pore structure. Development of ionic or electronic conductors with high charge mobility will be required to transmit the holes rapidly to the collecting electrode. Designing and developing novel materials and fabrication methodologies that are compatible for high-throughput, low-cost fabrication would also be useful.

Enhance Understanding of Nanostructured Photoelectrochemical Systems and Use the Knowledge to Establish and Control the Factors Governing the Efficiency and Stability of Nanostructured Sensitized Solar Cells

Theoretical and experimental studies should be aimed at understanding the phenomena determining light absorption, charge or exciton generation, charge separation, transport, recombination, and, ultimately, cell efficiency. Methodologies should be developed for forming ordered nanostructured, inorganic electrodes for optimum charge separation, and the effect of the resulting structures on the photoconversion properties should be investigated. Near-infrared absorbing molecular and quantum-confined sensitizers should be developed and studied. The stability of these sensitizers to ultraviolet and visible photolysis, moisture, and oxygen should also be studied. If the sensitizers degrade, approaches to suppress the photodegradation processes should be explored. Light management strategies should be investigated and exploited. Self-assembling molecular, supermolecular, and inorganic interface layers should be developed and studied. Factors determining the transport and recombination dynamics should be studied.

Incorporate Novel Third-Generation Concepts to Achieve Efficiencies Beyond the Shockley-Queisser Limit of 32%

To exceed the Shockley-Queisser limit, special light-harvesting (sensitizing) units, such as selected molecular sensitizers, and quantum-scaled structures (i.e., quantum dots) capable of generating charge carriers at a quantum yield greater than 100% must also be identified through detailed study. To fully utilize the usable regions of the solar spectrum, photon-energy up-conversion schemes (using, e.g., multijunction band-gap nanostructures and rare earth metal compounds) must be developed and understood. It will be important to understand the charge-carrier extraction and transport dynamics to enable the multiple excitons from quantum dots and charge carriers from oxidized sensitizers to escape recombination or deactivation and reach the collecting electrodes. It will be critical to identify and elucidate systems with long-lived intermediate charge-separated states and low-energy absorption bands. It will also be necessary to develop the basic knowledge base to create and eventually control the energetics for matching electronic band gaps and for tailoring the requisite optical properties or potential sensitizers.

Multijunction Multiphoton Devices

Multijunction nanostructured injection solar cells can be designed by appropriate choice of the absorber to absorb and quantitatively convert incident photons to electric current in selective spectral regions of the solar emission, while maintaining high transparency in the remaining wavelength range (see Figure 33). Absorbers (sensitizers in the case of dye-sensitized solar cells; other inorganic or organic compounds in the cases of nanowires, nanorods, nanocylinders, or organic bulk heterojunctions) with appropriate excitation energies and charge injection properties will need to be developed and characterized. Also, there will be a need to determine the fundamental factors influencing the incident photon-to-current conversion efficiency of the sensitized layer. The conditions for forming appropriate multilayered structures by techniques such as screen-printing, to facilitate the fabrication and optimization of multijunction structures, will need to be developed and studied.
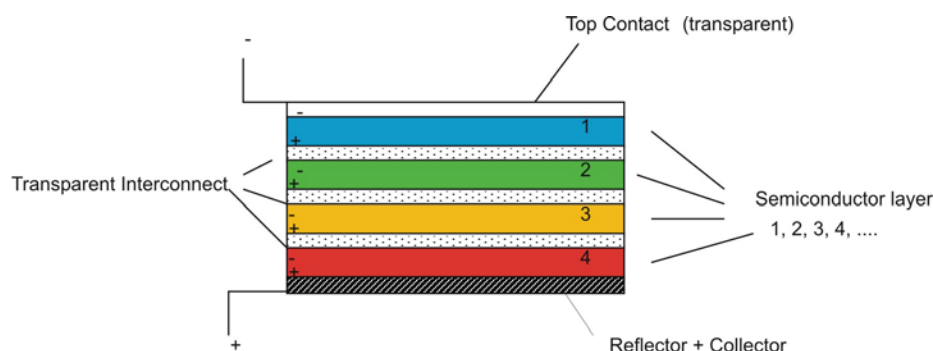

Figure 33 Quadruple junction solar cell comprising sensitized mesoscopic oxides of different color or thin-film photovoltaic cells as light-absorbing layers. The theoretical conversion efficiency of such a device is close to 50%.

Multiple Charge Carrier Generation

Calculated thermodynamic efficiency limits in single-junction solar cells (~32%) assume that absorption of an individual photon results in the formation of a single electron-hole pair and that all photon energy in excess of the energy gap is lost as heat. This limit, however, can be surpassed via multiple exciton (electron-hole pair) generation (MEG) by single-photon absorption as was predicted (Nozik 2002) and observed optically in PbSe and PbS quantum dots (Schaller and Klimov 2004; Ellingson et al. 2005). The ability to generate multiple charge carriers upon absorption of one photon could lead to greatly enhanced photocurrent and, ultimately, to very high efficiency solar cells.

SCIENTIFIC CHALLENGES

To move efficiencies towards a target of 50%, it is vital to address a number of fundamental scientific issues that include

- Control of nanoarchitecture,

- Light harvesting,

- Advanced light management,

- Control of charge separation and recombination,

- Control of charge carrier transport to the contacts,

- Design of multijunction systems, and

- Discovery of molecular routes to multiple carrier pair generation and photon up-conversion.

The fabrication of new nanostructured systems is opening up new possibilities for a range of devices, including batteries, sensors, and optoelectronics. Template synthesis methods using surfactants or block copolymers, for example, allow very precise control of the shape, size, and distribution of regular pores in oxide nanostructures. In addition, new methods for preparing highly organized nanostructures by chemical or electrochemical methods are showing considerable promise. Application of these exciting new developments to nanostructured photo-electrochemical solar cells will allow optimization of the different elements of functionality that are essential for high performance.

Light harvesting can be achieved by using strongly absorbing molecular dyes or semiconductor nanoparticles, nanorods, nanocylinders, or nanowires. Tuning of the absorption spectrum and energy levels of both types of sensitizer represents an important challenge. For efficient light harvesting, the absorption spectrum of the sensitizer needs to extend to the optimum band gap value of around 1.4 eV. At the same time, the energy levels of the sensitizer [highest occupied molecular orbital/lowest unoccupied molecular orbital (HOMO/LUMO) levels for dyes and valence/conduction band energies for semiconductor nanoparticles} must be fine-tuned to optimize the injection and regeneration steps. In the case of dyes, tuning can be achieved by modifying molecular structure, whereas size selection and surface modification can be used to tune semiconductor nanoparticles and nanowires. In both cases, it will be possible to enhance light-harvesting performance by using appropriate light management techniques.

Enhancing the performance of nanostructured solar cells requires understanding and controlling electron injection and subsequent recombination (either with the oxidized dye or with the "hole" in the contacting medium). The dynamics of these processes are sensitive to the interfacial structure and the molecular structure of the sensitizer. Exciting opportunities exist for the design of sensitizer molecules that incorporate the ability to remove the hole from the interface toward the bulk of the contacting phase before recombination can occur. In addition, core shell oxide structures can be used to control the rate of the electron injection and recombination processes at the interface.

Transport of electrons and holes in nanostructured solar cells plays an important part in determining cell efficiency. In the case of electrolyte-based cells, the competition between carrier collection and recombination places constraints on the thickness of the device that are much less stringent than those in other systems. However, when the electrolyte is replaced by an alternative hole-conducting medium, such as a molecular solid or polymer, recombination limits the

thickness to 1-2 μm. Enhancing charge transport in the two phases could help overcome this problem by ensuring that electrons and holes reach the contacts before they recombine. Potential strategies include fabricating ordered arrays of oxide nanopillars to speed up transport toward the substrate.

Potential molecular strategies to exceed the Shockley-Queisser limit include development of multijunction structures as well as new light-harvesting (sensitizing) units such as selected molecular dyes and semiconductor quantum dots that can generate multiple charge carrier pairs from single high-energy photons. Multilayer and multijunction nanostructured cells can be fabricated by simple techniques such as screen printing or doctor blading. The short-circuit photocurrent output of the layers can be readily matched by changing the film thickness and effective pore size.

The pursuit of high-efficiency cells should also include exploration of photon-energy up-conversion schemes (e.g., using multi-band-gap nanostructures, metastable electronic states, and long-lived charge-separated molecular states). An inherent advantage of nanostructured solar cells is that all of these strategies can be implemented by manipulation of the interface rather than the bulk.

POTENTIAL IMPACT

Successful research on nanostructured solar cells for renewable energy is particularly relevant to the solar energy technologies programs in the United States. Since nanostructures will potentially play a prominent role in many new approaches to photovoltaic conversion, the research is directly related to the National Nanotechnology Initiative, which crosses many federal agencies.

REFERENCES

R.J. Ellingson, M.C. Beard, J.C. Johnson, P. Yu, O.I. Micic, A.J. Nozik, A. Shabaev, and A.L. Efros, "Highly Efficient Multiple Exciton Generation in Colloidal PbSe and PbS Quantum Dots," *Nano Lett*. **5**, 865 (2005).

M. Grätzel, "Photoelectrochemical Cells," *Nature* **414**, 338 (2001).

M. Grätzel, "Perspectives for Dye-sensitized Nanocrystalline Solar Cells," *Prog. Photovoltaics* **8**, 171 (2000).

A.J. Nozik, "Spectroscopy and Hot Electron Relaxation Dynamics in Semiconductor Quantum Wells and Quantum Dots," *Annu. Rev. Phys. Chem.* **52**, 193 (2001).

A.J. Nozik, "Quantum Dot Solar Cells," *Physica E* **14**, 115 (2002).

R.D. Schaller and V.I. Klimov, "High Efficiency Carrier Multiplication in PbSe Nanocrystals: Implications for Solar Energy Conversion," *Phys. Rev. Lett*. **92**, 186601 (2004).

FUELS FROM WATER AND SUNLIGHT: NEW PHOTOELECTRODES FOR EFFICIENT PHOTOELECTROLYSIS

Photoelectrochemical systems have been demonstrated to robustly form hydrogen from water using sunlight. The known light absorbers, however, are either too inefficient (1–2%) in sunlight or too unstable in the field for practical implementation. New electrodes or electrode combinations, developed by a close coupling between theory and experiment, are needed to enable a robust, efficient system for direct solar-induced water splitting.

EXECUTIVE SUMMARY

Photoelectrochemical water splitting for hydrogen production, also known as photoelectrolysis, represents an advanced alternative to combining photovoltaic cells with an electrolysis system (Bard and Fox 1995; Khaselev and Turner 1998; Memming 2001; Nozik 1978; Nozik and Memming 1996; Licht 2002). The major advantage is that energy capture, conversion, and storage are combined in a single system. The solar energy, absorbed in a semiconductor electrode immersed in an aqueous solution, is used to produce storable fuels such as hydrogen (see Figure 34). In operation, the semiconductor collects the light energy,

Figure 34 Photoelectrolysis cell

then produces and directs the photogenerated carriers to a catalyst on the surface of the semiconductor where, depending on the semiconductor, either hydrogen, oxygen, or other photoproducts are produced. Other products are produced at a separate electrode that is either a metal or another illuminated semiconductor electrode. The water-splitting process has demonstrated high solar-to-hydrogen conversion efficiencies (>10%), but lifetime and cost issues remain to be solved.
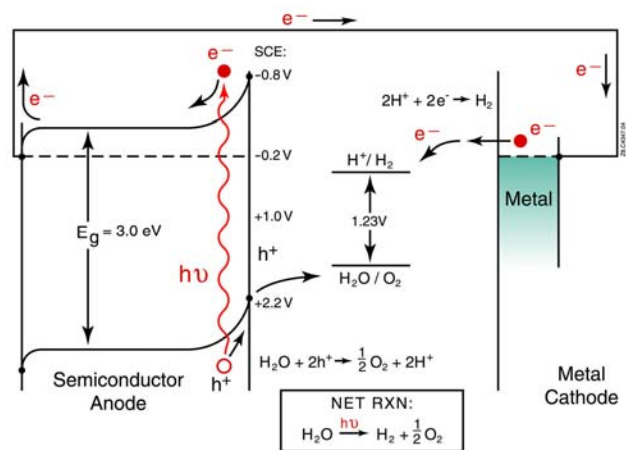
RESEARCH DIRECTIONS

Discovery of Photoelectrodes via Conventional Synthetic, Combinatorial, and Computational Methods

Discovery of semiconductors that have appropriate light absorption characteristics and are stable in aqueous solutions is a key issue. Efficient photoelectrolysis of water has been achieved by using expensive single-crystal III-V multijunction electrodes. However, concerns about the long-term stability of these systems and their high cost are significant issues. New theoretical and experimental approaches to discover photoelectrodes capable of photoelectrolysis reactions are needed.

Multicomponent structures are often needed when a special property needs to be optimized. High-temperature superconductors — in which the oxide with the current best transition temperature contains four metals ($HgBa_2CaCu_2O_{6+\delta}$, $T_c = 125$ K) — are a good example. A similar number of components may be necessary for water photoelectrolysis because the electrode must have structural stability, light absorption over much of the solar spectrum, and catalytic activity for the multielectron reactions required to produce useful fuels. When three or more components are needed, the number of possible combinations can be very large; therefore, a high-throughput technique capable of screening many compositions at once is required, because serial synthesis would not be fruitful on a reasonable timescale.

In the many years of research on light-induced water-splitting, researchers have not made use of the significant advances offered by first-principles electronic structure theory for screening novel semiconductors. Theoretical approaches have been developed to search for systems that satisfy well-posed target electronic properties; these include prediction of band gap and band energy positions, all based on alloy composition. Synergy between experiments and theory would provide predictive power to reduce the search space and enable researchers to better understand the properties of discovered phases that make them effective photoelectrolysis systems.

Configuration of Discovered Electrodes for Optimal Light Absorption, Carrier Collection, and Electrocatalysis

Mesoscopic Electrode Configurations. The band gaps of many of the stable oxides that have been used as photoelectrodes are so large that they do not absorb a large fraction of the solar spectrum. To address this shortcoming, researchers have made photoelectrodes by adding colored transition metal centers to high-band-gap oxides to absorb light in the visible region of the solar spectrum, or they have tried lower-band-gap oxides such as Fe_2O_3. The optical transitions between the bands formed by the transition metal centers in these materials are forbidden d-d transitions, resulting in low absorption coefficients in the visible region and leading to a rather high penetration depth of the light into the material. The large penetration depth of the light, and the fact that the carrier mobilities in oxides are generally lower than in conventional solar cell semiconductors, results in recombination of photogenerated carriers before they reach the semiconductor/electrolyte interface where the photoelectrolysis reactions occur.

Similar problems of low light absorption and carrier mobilities are overcome in the nanocrystalline TiO_2 photovoltaic cell. The light absorption is improved by creating a high-surface-area porous TiO_2 electrode covered with a light-absorbing dye. The light traverses many interfaces, so that when absorption occurs, the carriers are always near the interface; hence, carrier diffusion lengths are no longer a limiting factor. Nanostructured films, either with ordered domains (such as nanorods or nanowires) or with random domains of interpenetrating networks (also sometimes denoted as bulk heterojunctions), offer the opportunity to circumvent this key limitation. Similar approaches using either nanoporous films of active materials or particles of photon-absorbing and/or catalytic materials supported on a nanocrystalline scaffold are expected to yield high efficiencies for photoelectrolysis. Because no large crystals or crystallites are required, very low costs can be anticipated. In addition, these configurations lower the local current density for the electrolysis reactions, reducing overpotential losses. Back illumination

can be used to reduce the light scattering in the electrolyte caused by bubble formation when gases are evolved.

Multiple-band-gap Systems. A photoelectrolysis system could couple a p-type and an n-type semiconductor to drive photoreductions and photo-oxidations, respectively, where band gaps in the range of 1.0–1.2 eV for each electrode would be optimum; for a single-band-gap device, the optimum is in the range of 1.6–2.0 eV (see Figure 35). This approach provides extra voltage or driving force for photoelectrolysis, but it lowers the quantum yield by a factor of two. However, the two smaller-band-gap semiconductors can extend the utilization of the solar spectrum into the near infrared. Tandem configurations could be used, in which different band gap p-type and n-type electrodes are stacked so that the light impinges first on the higher-gap semi-conductor, where the high-energy photons are absorbed and converted to photo-products. The lower-gap semiconductor then absorbs the light passing through the higher-gap semiconductor to perform the complementary photoelectrolysis reaction. Material and device properties in multiple-band-gap systems require discovery of at least two semiconductors that must be configured to match the currents in the two electrodes to achieve optimum device efficiency.
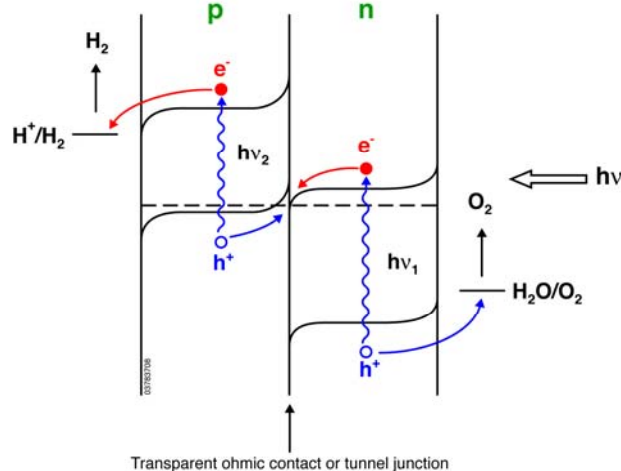

Figure 35 p-n Photoelectrolysis cell (photochemical diode). The n-type anode and p-type cathode are connected in a bi-layered monolithic structure through a contact that produces electron-hole recombination to permit charge balance. (Source: Nozik 1977)

SCIENTIFIC CHALLENGES

A high-throughput search for photoelectrolysis electrodes will produce libraries of new candidates that may also be useful for other scientific problems of relevance to energy conversion, such as fuel cell materials and catalysts. The coupling of computational science with experimental search techniques represents a new approach to exploration and discovery of new photoelectrodes with specific and unique properties.

POTENTIAL IMPACT

Successful research on new highly efficient, stable, and cost-effective photoelectrodes for photoelectrolysis represents a major advance in the critically important goal to produce hydrogen from solar energy and water, and hence, would help create the hydrogen economy. Storage of solar energy as useful fuels is needed to level out the demand cycle with the availability of sunlight.

REFERENCES

A.J. Bard and M.A. Fox, "Artificial Photosynthesis: Solar Splitting of Water to Hydrogen and Oxygen," *Accts. of Chem. Res.* **28**, 141 (1995).

O. Khaselev and J.A. Turner, "A Monolithic Photovoltaic-Photoelectrochemical Device for Hydrogen Production via Water Splitting," *Science* **280**, 425 (1998).

R. Memming, *Semiconductor Electrochemistry*. Wiley-VCH: Weinheim, Germany (2001).

A.J. Nozik, "Photochemical Diodes," *Appl. Phys. Lett.* **30**, 567 (1977).

A.J. Nozik, "Photoelectrochemistry: Applications to Solar Energy Conversion," *Annu. Rev. Phys. Chem.* **29**, 189 (1978).

A.J. Nozik and R. Memming, "Physical Chemistry of Semiconductor-Liquid Interfaces," *J. Phys. Chem.* **100**, 13061 (1996).

S. Licht (Ed.), *Semiconductor Electrodes and Photoelectrochemistry (Volume 6 of Encyclopedia of Electrochemistry)*. Wiley-VCH: Weinheim, Germany (2002).

LEVERAGING PHOTOSYNTHESIS FOR SUSTAINABLE SOLAR PRODUCTION OF BIOFUELS

Photosynthesis in plants provides a clear proof-of-concept of the ability to form fuels from sunlight. Use of the best-known plants would, however, require covering essentially all of the arable land on Earth to meet current global energy needs. Modification of the biochemistry of plants and bacteria, either genetically or through breeding, along with an understanding of the mechanisms by which natural systems produce fuel, is needed to improve the efficiency of such systems by a factor of 5–10 and to provide a convenient fuel for end use.

EXECUTIVE SUMMARY

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 materials, 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 useful organic molecules. These in turn can be bio-converted to a wide range of fuels and value-added chemicals. Through understanding and discovery, it is possible to increase solar energy-dependent biofuels production using plants and microbes. Challenges associated with achieving this goal include: (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 bioprocesses that constrain biofuels production due to photosynthetic sink limitations (i.e., biological control mechanisms that limit the conversion of energy from photosynthetic electron transport into chemical storage); (4) elucidating plant cell wall structure and understanding how it can be modified and efficiently deconstructed by protein assemblies; and (5) extending nitrogen fixation to biofuel crops to reduce dependence on fossil fuel nitrogen fertilizer.

SUMMARY OF RESEARCH DIRECTION

Photosynthesis provides >90% of the net input of energy into the biosphere. It produces the oxygen we breathe and drives the biogeochemical cycles. Photosynthesis generates reducing equivalents to convert inorganic materials to an organic form, produces cellular energy reserves (starch, cellulose and other polysaccharides, oils, polyhydroxybutyrate, etc.), and results in transmembrane gradients to drive bioenergetic pathways. The primary reactions of photosynthesis can operate at near-perfect quantum efficiency. The goal is to link these primary processes to produce useful chemical products and fuels. For example, the reduced ferredoxin produced as the major product of solar energy capture from Photosystem I can be used to drive the production of H_2 and methane production from CO_2.

PLANT PRODUCTIVITY AND BIOFUEL PRODUCTION

Broad implementation of biomass as an important energy source in the United States and in the world could potentially be facilitated by the genetic modification of plants for enhanced productivity, improving stress tolerance and minimizing exogenous nutrient inputs. Knowledge of the molecular and physiological mechanisms by which plants acquire drought, salt, or cold tolerance are likely to be important in permitting rational improvement of biomass crops. A related long-term objective is the incorporation of biological nitrogen fixation capability into non-legumes to improve the efficiency of plant production. The requirement for nitrogen fertilizer represents up to 25% of the cost of biomass production. Worldwide, approximately 160 million tons of NH_3 are produced annually by an energetically expensive fossil fuel-dependent process that could be displaced by biological nitrogen fixation.

CELL WALL BIOSYNTHESIS AND BIOFUEL PRODUCTION

Plant biomass consists largely of cell walls composed of polysaccharides and lignin, as shown in Figure 36. Relatively little is known about how the polysaccharides are synthesized or deposited during cell wall synthesis; most of the enzymes that catalyze synthesis of the major polysaccharides have not been characterized, and due to technical difficulties, essentially nothing is known about how wall polysaccharide composition is regulated. Recent advances in genomics and analytical chemistry have created new opportunities to make rapid progress in understanding how walls are synthesized and assembled.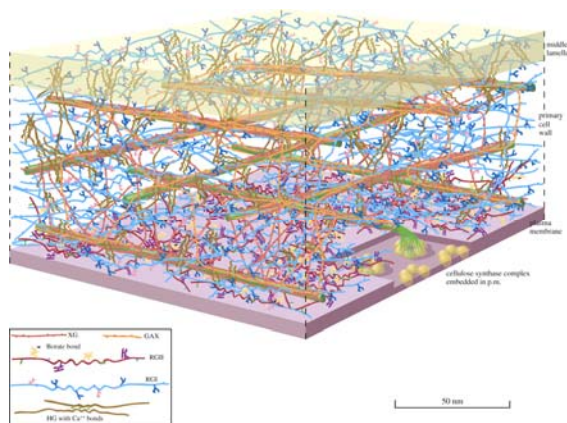 Additionally, new molecular imaging technologies may allow elucidation of the structure of assembled cell walls. The identification of the genes and corresponding enzymes involved in cell wall polysaccharide synthesis and assembly, and knowledge of the design principles, will create novel opportunities to genetically improve the composition of cell walls for various uses ranging from fiber applications to biofuels production. It seems likely that by altering the genetic control of cell wall composition, plants can be developed with significantly increased biomass accumulation. Additionally, cell wall composition can be tailored to meet various end uses related to different options in biomass processing for biofuels.

Figure 36 Model of plant cell wall (Source: Somerville et al. 2004)

MICROBES AND SOLAR BIOFUELS

Microorganisms represent a vast repository of biochemical diversity that remains largely unknown and untapped. Thirty to 50% of the coding capacity of microorganisms represents genes of unknown function, and less than 1% of all microorganisms can be cultivated in the laboratory. This biochemical diversity holds solutions for improving processes (e.g., cellulose or sugar transformations, lignin degradation, etc.) for biofuels production as well as the production

of high-value chemicals. Modern molecular techniques will enable improvements in existing biocatalysts. Research is needed to identify and maximize the function of genes and gene products identified through initiatives such as the Genomes to Life Program. Through metabolic modeling and genetic engineering, it will be possible to predict how to engineer the microbial metabolism, in particular that of photoautotrophs, for dramatic improvements in biofuels production (e.g., to enhance reductant delivery for biohydrogen production). With regard to gaseous biofuel production, the production of hydrogen in the biosphere is a very common phenomenon.

NEW SCIENTIFIC OPPORTUNITIES

Plant Productivity and Biofuel Production

To maximize efficient biofuel production, we need a deeper understanding of the control of carbon assimilatory processes at the biochemical, genetic, and molecular levels in plants and microbes. Maximum CO_2 fixation efficiency is directly linked to the energetics of the cell, and recent findings indicate that carbon assimilatory processes in bacteria are tied to control of the central pathways of nitrogen fixation, hydrogen production, and energy transduction. The photosynthetic efficiency of plants in converting solar energy into biofuel feedstocks is controlled not only by the intrinsic efficiency of photosynthesis but also by intricate genetic controls that determine plant form, growth rate, organic composition, and ultimate size. Thus, while the primary solar energy conversion efficiency of photosynthesis is as high as 5–10% under optimal conditions, the overall rate of photosynthetic CO_2 fixation is constrained by "sink limitations" — biological control mechanisms that limit the conversion of energy from photosynthetic electron transport into chemical storage. To improve the efficiency of solar energy conversion into biofuel feedstocks, it is critical to develop an in-depth understanding of the genetic controls of sink capacity and plant growth. Detailed knowledge of these mechanisms will be required to optimize solar interception, increase plant size, sustain storage capacity throughout the biofuel crop life cycle, and tailor the composition of biofuels for specific purposes.

CELL WALL BIOSYNTHESIS AND BIOFUEL PRODUCTION

Lignocellulose can be utilized for energy production in a variety of ways ranging from combustion to fermentation-based alcohol production. We need to understand how the chemical composition of cell walls impacts the efficiency of the various conversion technologies. In particular, there is a promising opportunity to modify the cell walls of biomass crops for production of liquid fuels by replacement of poorly utilized components, such as lignin, with structural polysaccharides. There are also important opportunities to improve the properties of the enzymes that degrade cell walls to fermentable sugars. Most fungi and some bacteria secrete a battery of enzymes that degrade polysaccharides and lignin to monomers that can be utilized as substrates for microbial growth. Additionally, cellulolytic microflora found in the rumen utilize a "cellulosomal" enzyme system comprised of complex scaffolds of structural proteins, which assemble outside of the cell and organize enzymatic subunits capable of hydrolyzing cellulose, hemicellulose, and other cell wall polysaccharides with high efficiency. Substantial progress has

been made in identifying and characterizing the various enzymes involved in microbial digestion of lignocellulose. However, in many cases, the enzymes or enzyme complexes found in nature are not well-suited to industrial-scale processes for conversion of lignocellulose to fermentable sugars and other useful chemicals. Progress in enzyme chemistry, structural biology, and computational chemistry have created exciting new opportunities to greatly improve the properties of enzymes for lignocellulose conversion. Additional investments in understanding the structure and function of polysaccharide and lignin hydrolyases will create significant improvements in the overall efficiency of lignocellulose conversion to liquid fuels. Additional research is also required to improve the efficiency with which sugars other than glucose are bioconverted to useful chemicals. Downstream processes for fermentation of cellulose degradation products are extremely important for biofuel production, and more work on maximizing these microbial processes is extremely important.

MICROBES AND SOLAR BIOFUELS

Globally, biological processes produce more than 250 metric tonnes of hydrogen per year. However, because other organisms in the biosphere rapidly use most of the metabolically produced hydrogen, this gas is not released into the atmosphere and the phenomenon of biological hydrogen evolution is not widely recognized. Algae and cyanobacteria employ the same basic photosynthetic processes found in green plants. They capture sunlight and use the energy to split water, release oxygen, and fix atmospheric carbon dioxide. All these microbes can adapt their normal photosynthetic processes to produce hydrogen directly from water using sunlight and the

Figure 37 Anaerobic phototrophs also produce hydrogen and are very active nitrogen fixers.

enzymes hydrogenase or nitrogenase. In anaerobic photosynthetic bacteria (see Figure 37), there are several enzymes that catalyze hydrogen metabolism and evolution, including reversible hydrogenases and the nitrogenase complex. In addition, some of these organisms can even couple the degradation of toxic halogenated compounds and lignin monomers to hydrogen production. While these capabilities have been known as laboratory curiosities for many years, only recently as the result of a number of advances in basic physiology, enzymology, protein structure, and molecular biology has the prospect of using these unique metabolisms as the basis for new energy-production technology become a possibility. The emerging tools and modern plant biology hold promise that significant amounts of global energy will be supplied by algal farms that access desert and coastal areas.
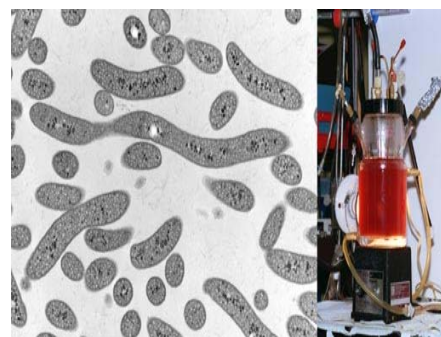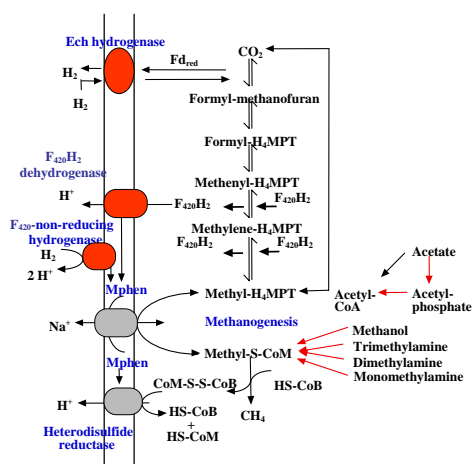

Figure 38 Mechanism of methanogenesis as currently formulated

In addition to hydrogen production, biological methane production (see Figure 38), is a well-

established biotechnology used worldwide, both to reduce waste biomass and to generate biogas fuel. Under anaerobic conditions, complex and largely undefined consortia of microorganisms depolymerize biopolymers and transfer the solar energy trapped by photosynthesis in these molecules into intermediate fatty acids, alcohols and methylamines. In the terminal reactions, methanogenic *Archaea* use hydrogen from fermentations to reduce carbon dioxide and methyl groups from the intermediates to generate methane. An integrated effort is needed to expand the application of anaerobes to a wider range of biomass and to construct microbial consortia that most efficiently convert the biomass to natural gas.

RELEVANCE AND POTENTIAL IMPACT

Modification of the biochemistry of plants and bacteria, either genetically or through breeding, along with an understanding of the mechanisms by which natural systems produce fuel, are needed to improve the efficiency of such systems by a factor of 5–10 and to provide a convenient fuel for end-use. The research directions identified here build upon advances in modern biology by the broader biological research community that can be directed toward substantial improvements in solar biofuels production. The new capabilities in computational chemistry, structural biology, molecular machines, and nanotechnology that have become available only recently will allow these ambitious goals to be reached.

REFERENCE

C. Somerville, S. Bauer, G. Brininstool, M. Facette, T. Hamann, J. Milne, E. Osborne, A. Paredez, S. Persson, T. Raab, S. Vorwerk, and H. Youngs, "Toward a Systems Approach to Understanding Plant Cell Walls," *Science* **306**, 2206–2211 (2004).

USING A BIO-INSPIRED SMART MATRIX TO OPTIMIZE ENERGY LANDSCAPES FOR SOLAR FUELS PRODUCTION

In photosynthesis, complex protein structures control and optimize energy flow in a dynamic fashion, leading to efficient solar energy conversion and storage. No artificial systems currently implement this approach in a useful fashion, and assembly of such systems is currently beyond the state-of-the-art for chemists. Development and use of smart matrices would revolutionize our ability to control and implement solar-fuel-forming systems at the molecular level.

EXECUTIVE SUMMARY

A central challenge for solar fuels production is the development of efficient new photocatalysts for solar energy capture, conversion, and storage. Biology has achieved the ideal of solar-initiated water-splitting coupled to chemical energy storage using abundant, renewable, self-assembling "soft" materials. The catalytic power and specificity that are key attributes of enzyme-mediated catalysis have their origins in the active environment provided by the protein. The proteins involved in the photosynthetic light-harvesting complexes and the reaction centers are not mere 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. This is a key feature of the natural system that allows it to operate efficiently. Current bio-inspired solar-energy conversion systems have been able to replicate in a limited fashion the light harvesting, directed energy transfer, and charge separation seen in photosynthesis. However, so far, this has been achieved by using strong covalent bonds to link the molecular components in the required configurations. Due to major limitations imposed by covalent synthesis of large assemblies, construction of the next generation of bio-inspired solar-energy conversion systems will require self-assembly of the molecular components into a "smart matrix" that controls their key electronic properties. Understanding how the smart matrix exercises dynamic control over the energy landscape of the active components within it is critical to optimizing solar energy conversion efficiency. This control extends from the attosecond-long electronic 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.

Achieving efficient solar-energy conversion systems using smart matrices will require (1) engineering proteins, polymers, membranes, gels, and other ordered materials to provide tailored active environments (i.e., smart matrices); (2) incorporating bio-inspired cofactors within the designed matrix; (3) integrating multiple cofactor-matrix assemblies to perform the overall function; (4) characterizing the coupling between the cofactors and the matrix in natural and bio-inspired systems using advanced techniques; (5) integrating experimental measurements of structural and electronic dynamics with multi-scale theoretical approaches to achieve fundamental breakthroughs in system design paradigms for solar energy capture and conversion by supramolecular structures; and (6) mapping out and predicting optimized electronic and structural energy landscapes for efficient formation of solar fuels.

SUMMARY OF RESEARCH DIRECTION

The key role played by the protein in regulating and facilitating the primary energy and electron transfer reactions of photosynthesis is best illustrated with reference to purple non-sulfur photosynthetic bacteria. In this case, the *same chemical entity*, bacteriochlorophyll, is used in the construction of both the light-harvesting complexes and the reaction centers. Whether a specific bacteriochlorophyll molecule is destined to fulfill a light-harvesting function or participate in electron transfer within the reaction center is solely controlled by the protein into which it is assembled. For example, the antenna proteins modulate the spectroscopic properties of the bacteriochlorophylls to increase the fraction of the solar spectrum absorbed. In addition, this wavelength programming, coupled with hierarchical structural organization, creates an energy funnel, which directs the captured energy downhill to the reaction centers. Within the reaction center, the protein controls the directionality of the electron-transfer and charge-separation processes, so that losses by wasteful deactivating recombination processes are prevented. Although we are now beginning to realize in general terms what the protein achieves, we do not understand how it achieves it.

The design of bio-inspired solar-energy systems is moving toward hierarchical supramolecular structures and their integration into interfacial host architectures as means to achieve control of light-initiated reaction sequences. This increase in structural complexity is also dynamic in nature. Molecular motions intrinsic to the individual molecular components are altered in the complex assembly; the resulting dynamics of the assembly most frequently dictate overall function, often in ways that are difficult to predict using current theoretical and experimental tools. Biology provides numerous examples of complex supramolecular structures with functions that are unexpectedly sensitive to minimally perturbative single-site mutations, or ones that show long-range cooperative effects. Molecular materials also show significant site-selective conformational sensitivities. For example, the nature of the connection between conductive molecules and metals dictates whether the molecule will behave as a molecular wire. From these examples, it can be anticipated that a definitive resolution of mechanistic function within complex bio-inspired supramolecular assemblies and the smart matrices in which they reside will require the application of new *in-situ* structural probes.

A grand challenge is to resolve structural and electronic dynamics over the full time scale of energy capture and conversion. At best, we currently have only a fragmentary understanding of the dynamic structural features of complex molecular systems in their electronic ground states. The complexities introduced by higher-order structures raise significant theoretical and experimental challenges that must be addressed by (1) the development of new theoretical concepts and predictive models for discovering structure-function relationships within biological, molecular, and supramolecular systems; (2) the *in-situ* determination of supramolecular structure and dynamics to resolve the dynamic interplay between supramolecular charge separation and host environments that are relevant to solar-energy conversion; and (3) the integration of theoretical and physical techniques to provide the knowledge necessary to achieve maximum photoconversion system performance. These research directions will exploit new, emerging methods for dynamic molecular structure determination, including multi-dimensional near- and far-field optical, vibrational, and magnetic spectroscopies; pulsed X-ray, neutron, and electron diffraction; and coherent scattering combined with multi-scale dynamic modeling.

NEW SCIENTIFIC OPPORTUNITIES

Making a Smart Matrix. A bio-inspired smart matrix must be able to promote (1) the conduction of holes and electrons over required distances and at moderate redox potentials, without significant losses; (2) the accumulation and storage of numbers of charges to enable chemical catalysis; (3) growth of the assembly in an ordered way from the nanoscale to the macroscale; and (4) compartmentalization of redox components and incompatible products, such as hydrogen and oxygen. In addition, a matrix that mediates a specific process (light harvesting, charge separation, chemical catalysis, etc.) must be compatible with integration into functional solar energy conversion systems.

Charge Transport in Dynamically Constrained Environments. When a charge separation reaction occurs in solution, it is well known that the newly formed charges interact with solvent dipoles in their immediate vicinity, leading to a reorganization of the overall orientation of the solvent molecules relative to the charged intermediates. This change in solvent orientation requires an energy penalty that may be reasonably large in polar media, which results in an overall slowing of the electron transfer rate. The protein in photosynthetic reaction centers provides an environment that dynamically adjusts to minimize the energy penalty as the charge-separation process occurs. Specific motions of individual amino acids may be critical in gating electron flow within the protein. In addition, the overall electrostatic environment of the protein provides a spatially tailored potential that promotes directional electron flow. This concept is illustrated schematically in Figure 39. It is important to understand which protein motions are responsible for this optimization, how to control this process, and how to adapt this process for use in bio-inspired artificial photosynthetic systems. This is a challenging problem that requires new techniques to probe molecular structure at the ultrafast time scales characteristic of these electron-transfer events.
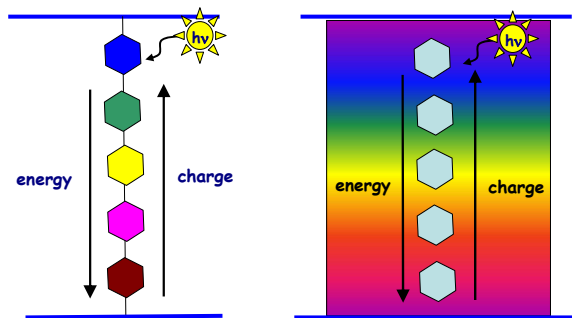

Figure 39 A smart matrix. Left: The present situation for transporting energy or charge with covalently linked, synthetically tuned chromophores. Right: Self-assembled chromophores whose properties are tailored by the smart matrix.

Proton-coupled Electron Transfer and Multiple Electron Transfers. In most biological redox processes, single electron-transfer events are followed by proton transfers that diminish the overall energy penalty paid by accumulating several negative charges in one location. Typically, the acid-base properties of the amino acids that are in the vicinity of the reduced species are involved in this process. It is often very difficult to discern the molecular details of proton-coupled electron-transfer processes, because the proton movements occur over short distances and x-ray structural probes are generally not capable of determining the positions of the protons. A major challenge is to find new ways to understand proton-coupled electron transfer and the structural requirements for minimizing the energetic requirements for such processes. New time- and spatially resolved probes for determining the mechanisms of these reactions are critical for

developing multi-electron catalytic sites in bio-inspired artificial photosynthetic systems for water oxidation and carbon dioxide reduction.

Controlled Assembly of Ordered Structures. The cofactors that carry out light harvesting and the primary charge separation in photosynthetic proteins are assembled at specific orientations and distances to provide optimized function. Moreover, the spatial relationship between the light-harvesting and reaction-center proteins is optimized for their mutual functioning. Knowledge of the ways in which these proteins assemble to give specific functional structures remains at an early stage of development. It is important to understand these processes in detail in order to apply them to the construction of systems that are hybrids of the natural system with modified redox components, and so that they can serve as a blueprint for self-assembly of bio-inspired artificial systems to minimize the synthetic effort required to produce the latter systems and at the same time provide enhanced functionality.

Compartmentalization of Incompatible Products. The formation of solar fuels requires reactions that produce both strongly oxidizing and strongly reducing intermediates. For example, the Photosystem II reaction center, along with the 4-Mn oxygen-evolving complex, generates redox potentials that are at the limit of what biomolecules can tolerate. Yet the protein provides an environment in the vicinity of these reactive intermediates that allows a useful number of catalyst turnovers to occur before accumulated damage results in the protein being replaced. At this point, very little is known about which protein environments will tolerate a particular reactive intermediate. Fundamental studies of active site design are necessary to be able to tailor specialized protective molecular compartments for all reactive intermediates to carry out their catalytic functions without being destroyed by reacting with their surroundings. This is a critical feature of catalyst design for both water oxidation and carbon dioxide reduction.

Structural Dynamics. Numerous remarkable advances are being made in the development of techniques that hold promise for achieving fundamental breakthroughs in imaging the atomic motions that control light-initiated reactions. These include emerging diffraction and spectroscopy techniques that exploit pulsed X-ray, neutron, and electron sources to resolve structural dynamics in a full range of crystalline, amorphous solid phase, and liquid phase materials. Paradigm shifts that occur with dynamic structural resolution are illustrated by a broad range of pioneering time-resolved X-ray diffraction and spectroscopy studies that are emerging for imaging structural dynamics linked to photochemistry. For example, recent 100-ps time-resolved crystallographic studies of myoglobin have revealed the atomic reorganization events coupled to porphyrin-bound CO photolysis and identified the unexpected appearance of the CO across the porphyrin plane (see Figure 40). Equally important are advances in the application of time-resolved X-ray spectroscopies and coherent and incoherent scattering in non-crystalline materials. New pulsed X-ray, neutron, and electron sources are providing opportunities to extend pump-probe X-ray techniques to the picosecond and femtosecond time-domains. Extrapolation of these techniques to include *in-situ* resolution of structural dynamics coupled to solar-fuels production in the non-crystalline media most relevant to solar-energy conversion offer entirely new opportunities for breakthroughs in resolving the structural basis for energy-conserving function in both natural and artificial photosynthesis.
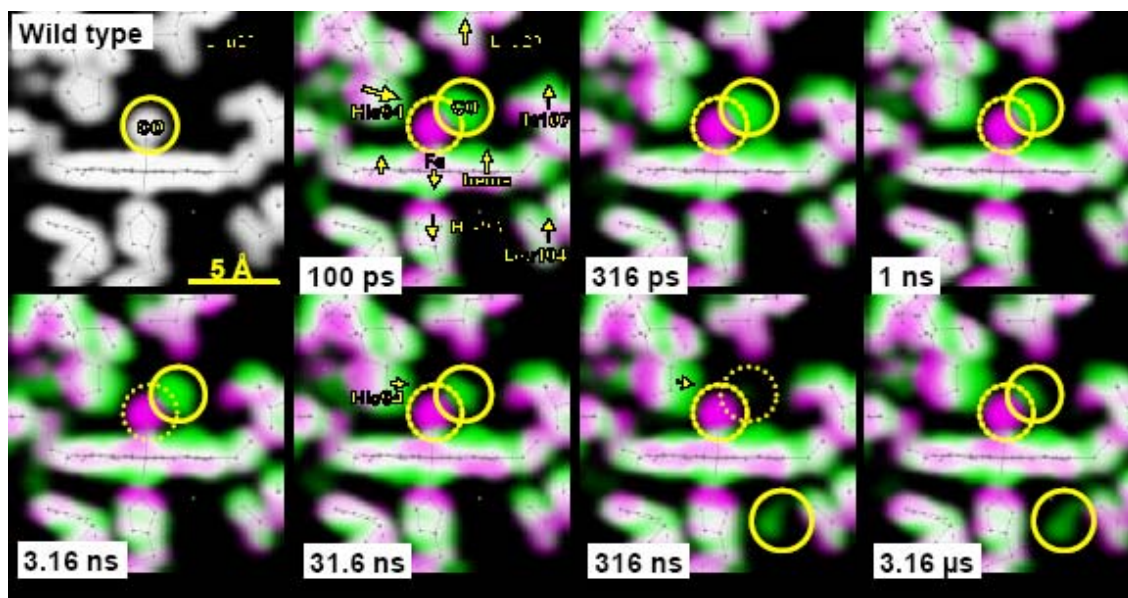
Figure 40 X-ray diffraction determined snapshots with 100-ps time-resolution of atomic motions coupled to CO photolysis in myoglobin, achieved using pump-probe X-ray crystallographic techniques (Source: Schotte et al. 2004)

Recent work has demonstrated the critical need for structural techniques to resolve the local site electronic or nuclear motions responsible for gated electron transfer in reaction centers that cannot be detected with crystallographic techniques as typically applied to photosynthetic proteins (see Figure 41). The increasing complexities of supramolecular solar-energy-converting assemblies, and the sensitivity of light-initiated chemistry to the details of structure and dynamics in molecular and host environments, suggest that similar limitations may ultimately be reached with bio-inspired supramolecular structures. The promise of breakthroughs can be envisioned by combining information from diffraction approaches with advances in the application of multi-dimensional magnetic, vibrational, and optical spectroscopies for mapping dynamic electron and nuclear coupling during the time-course of photochemical reactions. These approaches, combined with *in-situ* near-field and atomic probe techniques, offer promise to achieve breakthroughs in the visualization of mechanisms for site-specific, microscopic control of solar-energy conversion.

Figure 41 Light-induced Fourier difference maps adjacent to the Q_b site in *B. viridis* reaction centers (Source: Baxter et al. 2004)

Electronic Dynamics. Opportunities to directly image the electronic dynamics most intimately linked to solar-energy capture and conversion processes are demonstrated by advances in coherent and energy-loss X-ray and optical spectroscopies. Recently, an elegant demonstration of the ability for multi-dimensional, coherent electronic absorption spectroscopies to resolve dynamic electron
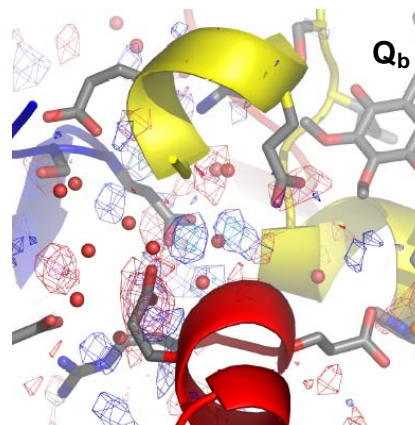
coupling in multi-cofactor-containing assemblies has used 2-D transient optical spectroscopy to map the time evolution of coupled electrons in light-harvesting proteins (see Figure 42). The crystal structures of these light-harvesting proteins show impressively large arrays of cofactors. The complexities of these arrays and their protein hosts prevent a definitive determination of structure-based function and elucidation of underlying design principles. Two-dimensional transient optical and related coherent spectroscopies offer new approaches for achieving breakthroughs in understanding the design and function of multi-cofactor arrays. These spectroscopies are well-suited for extension to *in-situ* analysis of cofactor arrays within specialized micro-environments.

Building upon these coherent optical techniques are emerging analogous X-ray spectroscopic techniques for deciphering electronic structure at metal centers and finer, higher-resolution length scales. Pioneering examples include inelastic X-ray scattering techniques that have imaged spatial and temporal electric-field-induced electron density disturbances associated with charge and electric-field perturbations in water with 40-attosecond (10^{-18} s) time resolution (Abbamonte et al. 2004). These measurements allowed mapping of electronic disturbances calculated to be produced by an oscillating molecular dipole and diffusing ion fields. These studies suggest unprecedented opportunities to map the dynamic electronic responses of solar-fuel-producing materials.

Multi-scale Theoretical/Computational Approaches. The complex nature of supramolecular assemblies associated with a variety of host architectures and the anticipated explosion in experimental detail concerning light-initiated electronic and nuclear dynamics raise significant theoretical challenges. New, multi-scale theoretical/computational methods are critically needed to account for the complexities of excited-state energetics applied across multiple spatial length scales relevant to supramolecular structures within complex host architectures, and on the range of time scales encompassing solar-energy capture, conversion, and storage. New theoretical methods are essential for establishing predictive methods to accelerate the design of efficient systems for solar fuels production.
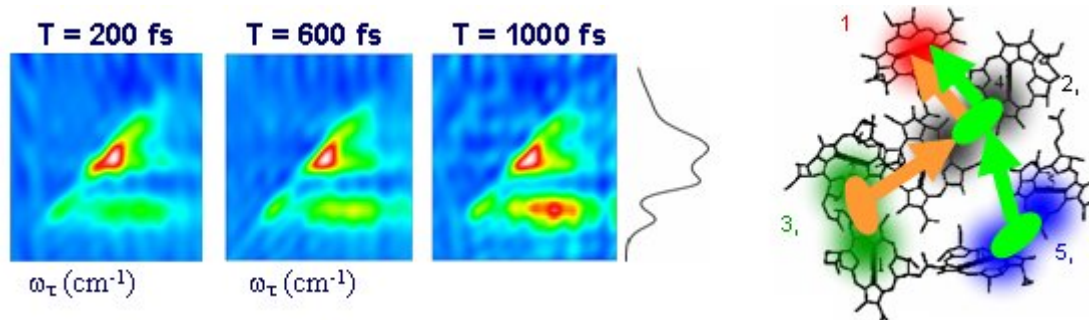

Figure 42 Dynamically resolved electronic coupling in the FMO protein using 2-D pulsed spectroscopy (Source: Brixner et al. 2005)

RELEVANCE AND POTENTIAL IMPACT

The development and use of smart matrices would revolutionize our ability to control and implement solar-fuel-forming systems at the molecular level. The discovery of the fundamental design principles needed to maximize the efficiency of photoconversion by bio-inspired molecular and supramolecular structures would make it possible to tailor the performance of each module in a solar-fuels production system to its specific function. The flexibility of a modular approach would translate into economic advantages as well, because individual modules could be optimized as advances in science and technology permit.

REFERENCES

P. Abbamonte, K.D. Finkelstein, M.D. Collins, and S.M. Gruner, "Imaging Density Disturbances in Water with a 41.3-attosecond Time Resolution," *Phys. Rev. Lett.* **92**, 237401–237401/4 (2004).

R.H.G. Baxter, B.-L. Seagle, N. Ponomarenko, and J.R. Norris, "Specific Radiation Damage Illustrates Light-induced Structural Changes in the Photosynthetic Reaction Center," *J. Am. Chem. Soc.* **126**, 16728–16729 (2004).

T. Brixner, J. Stenger, H.M. Vaswani, M. Cho, R.E. Blankenship, and G.R. Fleming, "Two-dimensional Spectroscopy of Electronic Couplings in Photosynthesis," *Nature* **434**, 625–628 (2005).

F. Schotte, J. Soman, J.S. Olson, M. Wulff, and P.A. Anfinrud, "Picosecond Time-resolved X-ray Crystallography: Probing Protein Function in Real Time," *J. Struct. Biol.* **147**, 235–236 (2004).

SOLAR-POWERED CATALYSTS FOR ENERGY-RICH FUELS FORMATION

All methods of producing solar fuels must involve coupling photo-driven single electron steps with fuel-forming, multi-electron transfer processes. No inexpensive, man-made systems come close to the performance of naturally found enzymes, which perform such processes with high turnover and minimal energy loss. Practical solar fuel formation requires construction of currently unknown catalyst systems to form hydrogen and oxygen from water and to efficiently reduce carbon dioxide from the air.

EXECUTIVE SUMMARY

Significant scientific challenges confront the design and synthesis of efficient, high-turnover, solar-powered catalysts for the conversion of solar energy into energy-rich fuels. Important reactions include the splitting of water into oxygen and hydrogen and the reduction of carbon dioxide to methane. Guideposts for the development of new systems will come in part from the understanding acquired from bioenergetic proteins involved in fuel-producing reactions, especially the water-splitting reaction of Photosystem II and hydrogen-producing reaction of hydrogenase. The performance of the current generation of catalysts is far from that required for a solar fuels production system with even modest efficiency, so that the development of a new generation of fuel-forming catalysts is necessary for integration into both higher-order artificial photosynthetic assemblies and photoelectrochemical devices. To achieve this objective, several important goals must be attained: (1) identify new methods for unraveling the mechanisms of complex, coupled reactions for the solar production of fuels; (2) develop a fundamental understanding of excited-state bond making and breaking processes yielding oxygen and hydrogen; (3) understand the rates and mechanisms of multielectron/atom transfer reactions using new theoretical and experimental approaches; (4) understand how proton-coupled electron transfer reactions including H atom and hydride transfers reduce the energy requirements for catalytic processes; (5) understand at a molecular level how catalytic reactions occur at interfaces and surfaces; and (6) develop molecular design and synthesis strategies to produce robust functional catalytic systems that mimic biological processes.

SUMMARY OF RESEARCH DIRECTION

Any practical technology for the decomposition of water into hydrogen and oxygen needs to circumvent the need for sacrificial reagents (i.e., those that are consumed and are not part of a catalytic cycle). Fabrication of all of the components for large-scale solar energy utilization must be inexpensive, a requirement arising from the large surface areas needed for future solar fuels plants. Most of the catalysts that have been explored are based on noble metals that may be too expensive for practical deployment. It is therefore important to use catalysts that are based on the first-row transition metals. Biological catalytic systems demonstrate that this is an achievable goal. The catalyst must be robust, having a high turnover coefficient, rapid cycling, and chemical stability under the harsh conditions of prolonged irradiation. A practical catalyst should consist of synthetically accessible components with favorable physical characteristics, such as solubility,

low toxicity, and processibility. To meet these challenges, the tools of theory and experiment must be brought together to understand and control catalytic processes.

Blueprint for Fuel-forming Catalyst Design

The essential requirements for electron-transfer driven, catalyzed production of solar fuels (such as H_2 or a carbon based liquid fuel) are captured in Figure 43. The left-hand system features the oxidation of water, and the right-hand side features (for purposes of illustration) reduction of CO_2 to formic acid. Such systems share common features and illustrate a generic, systems approach to successful catalyst design. The essential elements are as follows.

(1) **An electron transfer interface.** Catalyst systems for oxidation or reduction are driven by electron transfer to or from an electron transfer interface. The source of electrons is generic, potentially from molecular excitation-electron transfer, a photovoltaic source, or even the excitation-electron transfer apparatus of the natural photosynthetic apparatus.

(2) **Proton-coupled electron transfer (PCET) for redox leveling and proton addition or removal.** The gain or loss of protons, which prevents the accumulation of charge, is required for multi-electron transfer in order to avoid high-energy proton intermediates, thereby reducing reaction barriers.

(3) **Catalysis via atom, ion transfer, bond formation and breaking.** The key elements at this site are the utilization of atom (e.g., O or H) or ion (e.g., H⁻) transfer reactions that carry out the complex chemical transformations required with reaction barriers sufficiently low to ensure facile reactions on the sub-millisecond time scale. All of these elements must be spatially arranged to couple efficiently to ultimately generate fuel.
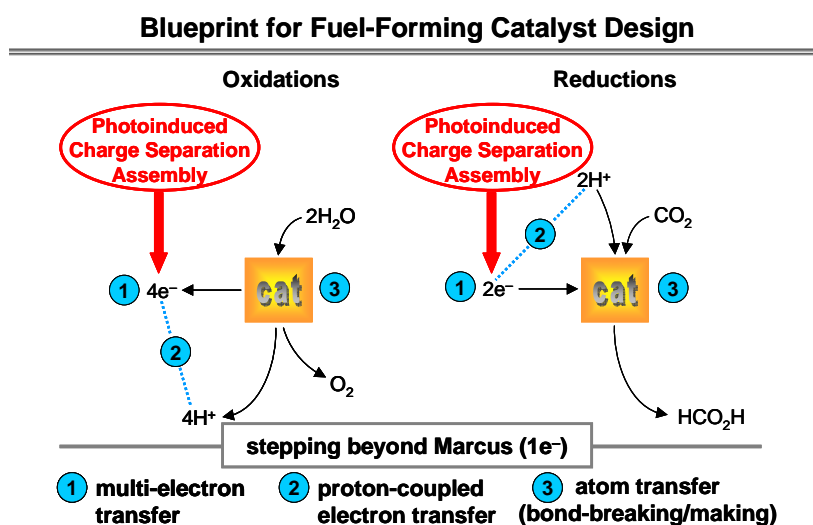

Figure 43 A blueprint for catalyst design detailed for both oxidation and reduction catalysts (Cat = catalyst)

While these essential features of catalyst design are widely recognized, the fundamental knowledge base needed to control the steps following electron transfer is almost completely lacking.

NEW SCIENTIFIC OPPORTUNITIES

Mechanisms of Complex, Coupled Reactions for the Solar Production of Fuels. It is evident from the very limited number of active non-biological catalysts discovered that reactions essential to solar production of fuels are exceedingly complex and require precise control of molecular events. Structures that promote the coupling of productive reactions and suppress those that are unproductive must be developed and refined. Mechanistic studies are therefore essential to the rational design of advanced catalytic systems. This understanding can be achieved by the isolation and structural/dynamical identification of reaction intermediates using a combination of techniques ranging from classical spectroscopic, electrochemical and magnetic analysis to transient spectroscopy and mass spectrometric/dynamical analyses using isotopic labeling. One example of the power of combining these diverse techniques is the level of understanding recently achieved in the catalytic conversion of H_2O to O_2 catalyzed by binuclear ruthenium μ-oxo complexes.

Excited-state Bond Making and Breaking Processes. Photochemical bond breaking and bond making reactions of many inorganic and organometallic compounds can directly lead to end products in fuel production, including hydrogen from water and carbon dioxide reduction products. Light-induced reactions are of interest because they can provide reaction paths that are not accessible to ground states. The fundamental principles for developing new photosystems for product formation exist for photo-driven inorganic and organometallic substances. Research is needed to optimize photoreaction quantum yields. To accomplish this, a better understanding of excited-state decay pathways in promising complexes is needed in order to channel excitation energy into the fuel-producing reaction paths. These efforts can be enhanced by the development of more accurate excited-state electronic structure calculations.

Theoretical and Experimental Studies of Rates and Mechanisms of Multielectron/atom Transfer Reactions. There is a need for a systematic theory of atom and ion transfer, which is analogous to the Marcus theory of electron transfer. This theory will emanate from and be tested by systematic kinetics studies. In addition, mechanisms must be understood and developed for redox leveling (as occurs in biological systems) as well as for coupling single and multiple electron transfer reactions. A critical aspect of this development is the design of robust ligand systems for sustained multiequivalent chemistry.

Proton-coupled Electron Transfer Reactions Including H Atom and Hydride Transfers. Photochemical H_2O and CO_2 reduction to fuels poses scientific challenges including proton-coupled multielectron transfer processes. For example, a number of photosynthetic systems show promise in the photoreduction of CO_2 to CO and/or formate, however, systems that demonstrate the transformation to methanol (with 6 protons and 6 electrons) or methane (with 8 protons and

8 electrons) are extremely limited. New approaches to hydride and hydrogen atom transfer need to be developed. Theoretical studies of mechanisms, structures of intermediates, and transition states are needed to augment experimental work. New theoretical treatments are also needed to handle multi-body and strongly coupled electron-nuclear events.

Catalytic Reactions at Interfaces and Surfaces in Order to Understand These Reactions at a Molecular Level. Catalytic mechanisms must be understood at a molecular level when the catalyst is present at an interface or on a surface. This understanding should include the development of both catalysts and techniques that permit the detection and study of all the intermediates relevant to the catalytic process and their reaction sequence, kinetics, and energetics.

Synthesis of Robust Functional Catalysts that Mimic Biological Processes. A combination of techniques (ranging from X-ray crystallography and magnetic resonance spectroscopies to genetic engineering) can elucidate the structure and dynamics of the intermediates of catalytic reactions occurring at redox centers of key enzymes, such as Photosystem II, involved in solar energy conversion. This knowledge is necessary to identify the precise molecular mechanisms of these biological processes. Guided by this knowledge, effective catalysts for water oxidation and carbon dioxide reduction must be synthesized, tested, and optimized. Targets include polynuclear metal systems and particularly metals that can replace high-cost noble metals as catalysts.

RELEVANCE AND POTENTIAL IMPACT

Practical solar fuel formation requires construction of currently unknown catalyst systems to form hydrogen and oxygen from water and to efficiently reduce carbon dioxide from the air. The development of water oxidation and carbon dioxide reduction catalysts will provide non-polluting fuels, namely hydrogen and hydrocarbons, from readily available feedstocks. Burning hydrogen results only in the production of water, while burning hydrocarbon fuels made from carbon dioxide provides a closed cycle that does not increase the carbon burden in the atmosphere.

BIO-INSPIRED MOLECULAR ASSEMBLIES FOR INTEGRATING PHOTON-TO-FUELS PATHWAYS

Molecular systems that mimic the photoconversion steps of photosynthesis have been synthesized using complex and costly sequences of chemical reactions. Yet, modular systems that avoid these difficulties by self-assembling into complete artificial photosynthetic systems remain largely unknown. 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.

EXECUTIVE SUMMARY

A scientific grand challenge is making bio-inspired, molecular assemblies that integrate light absorption, photo-induced charge separation, and catalytic water oxidation/fuel formation into a single fully functional 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 reaction centers. 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 fuel production occur. The self-organization of molecular structures using a variety of nanoscale motifs must be implemented to make these processes highly efficient. 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 to give rise to ordered structures. Achieving the goal of producing a functional integrated artificial photosynthetic system for efficient solar fuels production requires: (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; and (3) understanding and controlling the reactivity of hybrid molecular materials on many length scales.

SUMMARY OF RESEARCH DIRECTION

Innovative Architectures for Coupling Light-harvesting, Photoredox, and Catalytic Components

Research into the design and synthesis of molecular systems comprised of chromophores, electron donors, and acceptors, which mimic both the light-harvesting and the charge separation functions of photosynthetic proteins, has clearly demonstrated that covalent systems can perform these functions. In addition, catalysts for fuel-forming reactions are also based largely on covalently linked molecules, even though they are less well developed. However, what remain

largely unknown are the fundamental concepts of how to prepare individual light-harvesting complexes, reaction centers, or catalysts that can readily engage in specific intermolecular interactions promoting their assembly into ordered supramolecular structures with the ability to function as complete artificial photosynthetic systems. It is a major scientific challenge to develop small, functional building blocks, having a minimum number of covalent linkages, which also have the appropriate molecular recognition sites that facilitate self-assembly into complete, *functional* artificial photosynthetic assemblies.

The construction of an integrated artificial photosynthetic system will be achieved through hierarchical organization of molecular and supramolecular constructs. The synthesis of molecular building blocks allows very fine control over the chemistry and physics of energy and electron transfer. This is required for the first steps of solar energy conversion because the excited states and initially formed, charge-separated states are thermodynamically and kinetically prone to reactions that convert the stored solar energy to useless heat. Self-assembly, or supramolecular organization, on the other hand, provides a facile mechanism for assembling large numbers of molecules into structures that can bridge length scales from nanometers to macroscopic dimensions. It can also lead to synergistic and *emergent* properties that are not intrinsic to the building blocks themselves. For example, the ability of the light-harvesting antenna illustrated in Figure 44 to form ordered aggregates elicits self-assembly of a reaction center at which charge is separated following photoexcitation.

Figure 44 The red perylenebis(imide) dyes function both as antenna molecules and as self-assembly points, which bring the two green perylenebis(imide) dyes close enough to form a dimer within which ultrafast charge separation occurs. (Source: Rybtchinski et al. 2004)

Visible light-driven water-splitting or CO_2 reduction with high efficiency is currently achieved only in the presence of sacrificial reagents. The conversion of H_2O to H_2 or O_2, or of CO_2 to a liquid fuel like methanol requires two or more visible quanta. The reasons for the inefficiency in the absence of sacrificial donors or acceptors involve adverse processes that occur upon absorption of a photon: spontaneous back-reaction, trapping of excitation energy or migrating charge by defects or impurities (semiconductors), unwanted chemical reactions due to lack of materials robustness, and lack of separation of intermediates and products. The design of new self-assembled photocatalysts that eliminate the need for sacrificial reagents is imperative for achieving efficient solar fuel production. The challenge is to develop assemblies that afford coupling of the active components for efficient solar to fuel conversion without the need of sacrificial reagents. These assemblies currently do not exist.

Understanding the Relationships between Electronic Communication and the Molecular Interactions Responsible for Self-assembly

Hierarchical structures that provide directional organization on different length scales can be prepared by molecular self-assembly. While individual interactions between covalent molecules, such as a single hydrogen bond, are generally too weak to maintain the structure of a supramolecular assembly, several such interactions with proper design can lead to robust
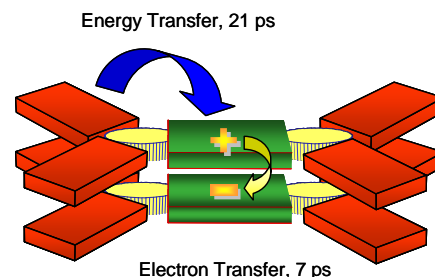
structures. Supramolecular organization can lead to a diversity of structures, some of which are highly symmetric with repeating patterns. Such motifs are useful for the construction of antenna units and molecular conductors. However, repeating patterns will not by themselves lead to functional devices. The reason for this is that the supramolecular assemblies required for an artificial photosynthetic system must not be simply structural, but also *functional*. They must provide pathways for migration of light excitation energy among antenna chromophores, and from antennas to reaction centers. They must also incorporate charge-conduction devices, or molecular "wires" that can efficiently move electrons and holes between reaction centers and catalytic sites. Discovering the principles governing excitation and charge migration within supramolecular assemblies is a major scientific challenge. The supramolecular assembly must not only facilitate and correlate directional flow of energy and charge within the integrated solar conversion device, but also provide an environment that preserves the functions of the individual components (antennas, reaction centers, catalysts) and protects them from damage.

The overall organization of the integrated devices must also provide mechanisms for transport of oxidizing and reducing equivalents across phase boundaries. This includes functionally interfacing molecules with traditional materials such as conductors and semiconductors so that charge transport across the boundaries is highly efficient. Phase boundaries provided by lipid bilayers, micelles, nanoparticles, polymers, and similar systems offer mechanisms for separating molecular redox equivalents, fuel molecules, and oxidizing agents. This can prevent charge recombination and destruction of fuels by oxidizing materials. Finally, the supramolecular organization must also provide an environment that separates the final products of the fuel production process (e.g., H_2 and O_2), and allows for their extraction and transport. A recent example of a hybrid system that carries out proton pumping using both artificial and natural building blocks incorporated into a liposome is shown in Figure 45.
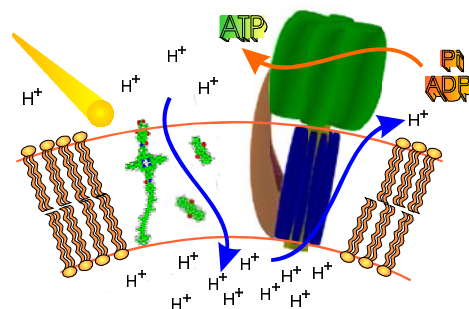

Figure 45 Hybrid light-driven proton pump using charge separation within a donor-acceptor triad and ATP synthase incorporated into a liposome (Source: Steinberg-Yfrach et al. 1998)

Understanding and Controlling the Reactivity of Hybrid Molecular Materials on Many Length Scales

Supramolecular structures can cover many length scales, which allows integration of individual molecules into nano- or meso-scale structures that can carry out the entire solar fuels production process. Biological systems employ a hierarchical organization to carry out many functions, including those of photosynthesis. Chemical processes such as microphase separation in block copolymers, template directed sol-gel synthesis of porous materials, layer-by-layer synthesis, nanoscale imprinting and patterning, and particle self-assembly have opened the door to a huge variety of hierarchical structures that are organized on several length scales. The challenge is to map these new synthetic techniques onto the demands of artificial photosynthesis in order to better control light-harvesting, charge separation, traffic control of holes and electrons, catalytic reactions, and permanent separation of the photo-generated fuel and oxidant. Tasks include the development of novel methods for compartmentalizing oxidizing or reducing sites by

nanostructure design, and development of nanoscale pore architectures that steer reaction intermediates to desired fuel products. Such assemblies could be developed in the form of nanoporous membranes, in effect producing an artificial "leaf."

Multi-junction solar cells convert light to electricity across the solar spectrum, and are the highest-efficiency solar conversion devices known. In these devices, high quantum efficiency is achieved only with epitaxially grown single crystal heterojunctions, which are prohibitively expensive to produce. The analogous nanocrystal heterojunction devices either do not exist, or have not yet been tested as solar photoconversion devices. However, nanomaterials offer many potential advantages for solar cells, such as the low cost of single crystal synthesis, tolerance for lattice mismatch in junctions, and the ability to control three-dimensional architecture through shape-controlled growth, microphase separation, and layer-by-layer synthesis. Novel architectures such as branched nanocrystals, nanowires, nanoribbons, and nanotubes provide useful building blocks for coupling of light-harvesting and photocatalytic components into functioning photocatalytic assemblies. The challenge is to design these assemblies to drive energetically demanding reactions, such as water-splitting, by using visible and near-infrared light.

NEW SCIENTIFIC OPPORTUNITIES

The design and preparation of an integrated, molecule-based system that will convert sunlight into useful fuels is a challenging goal. However, natural photosynthesis has already achieved this goal within the context of the biological world. By understanding the natural process and exploiting it in artificial constructs, it will be possible to construct artificial photosynthetic systems maximized for production of fuels useful to human society.

Understand the Dependence of Excitation Energy and Charge Flow on Molecular Structure and Intermolecular Boundaries from the Molecular to the Device Scale

A major scientific challenge is to develop a complete understanding of how weak, non-covalent, associative interactions, such as hydrogen bonds and π-π interactions, promote or inhibit energy and charge flow across molecular boundaries. This is critical to achieving an integrated artificial photosynthetic system because formation of a *functional* system by self-assembly of building blocks requires controlled energy and charge flow across the weak associative points of molecular contact. Studies are also needed on nanostructured and self-assembling junctions (e.g., at semiconductor nanocrystal/polymer and polymer/polymer interfaces) to understand the effects of composition, dimensionality, and overall architecture on the dynamics of excitons and charge carriers. In addition, to design better interfacial catalysts for water oxidation and fuel formation, the detailed molecular understanding that is being developed for molecular catalysts needs to be translated to surface-bound and colloidal catalysts. This requires the development of time-resolved structure-specific spectroscopic tools (vibrational, X-ray Absorption Fine Structure [XAFS], etc.) with very high sensitivity to identify transient intermediates and catalyst structural changes under reaction conditions. Theory and computational tools must also be developed to assist experimental studies with the goal of identifying active sites on surfaces with atomic precision.

Develop Charge Transport Structures to Deliver Redox Equivalents to Catalysts

Structured assemblies need to be developed that promote organization of the active units (light-harvesting, charge-conduction, catalytic) to optimize coupling between them for efficient fuel production. Molecular linkages, such as molecular "wires," need to be developed for efficient charge conduction between catalytic sites and photoactive components embedded in the assembly. For example, one class of such assemblies is 3-D mesoporous inert supports that allow precise spatial arrangement of the active components in a predetermined way for optimum coupling and protection from undesired chemistries. These supports must have structural elements (walls, membranes) that allow separation of primary redox products on the nanometer scale to prevent undesired cross-reactions and facilitate prompt escape of the products from the fuel-forming sites. Catalytic sites should be separated in such a way that energy-rich products, such as H_2 and O_2, cannot recombine thermally. A few molecular catalytic components are currently available for multi-electron H_2O and CO_2 activation, but methods are lacking that allow coupling of these components to electron/hole conducting moieties in 3-D frameworks.

Couple Single Photon Events to Accumulation of Multiple Redox Equivalents

In most cases, the absorption of light by a chromophore leads to the production of a single electron-hole pair. However, fuel-forming reactions involve the formation of covalent bonds, which are formed from electron pairs. Thus, an integrated solar fuels production system must accumulate electrons from single-photon events and deliver them to the site of fuel molecule formation. An excellent example of this function is the water oxidation catalyst of photosynthesis, which can accumulate the oxidation equivalents needed to split water. There has been very little research along these lines in molecule-based systems, and finding practical ways to accumulate redox equivalents at a particular molecular site is a major scientific challenge.

Develop Control Elements that Modulate Energy and Charge Flow between Active Components

Photosynthesis incorporates control elements that maximize photosynthetic performance under low light conditions and protect the photosynthetic apparatus during times of very high light intensity that could lead to photodamage. Integrated artificial photosynthetic systems for solar fuel production will ultimately need similar built-in control elements. For example, in times of excessively high light intensity, antennas could be decoupled from charge-separation centers, and the excess light energy degraded to heat or emitted as fluorescence in order to prevent photodamage. It is also necessary to create architectures that actively partition excitation energy absorbed by an antenna among different reaction centers in order to maintain each reaction center at maximum efficiency.

RELEVANCE AND POTENTIAL IMPACT

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. Developing such an integrated system would have a major impact on energy supply worldwide, as well as provide a new paradigm for designing all new molecular energy conversion systems.

REFERENCES

B. Rybtchinski, L.E. Sinks, and M.R. Wasielewski, "Combining Light-harvesting and Charge Separation in a Self-assembled Artificial Photosynthetic System based on Perylenediimide Chromophores," *J. Am. Chem. Soc.* **126**, 12268–12269 (2004).

G. Steinberg-Yfrach, J.-L. Rigaud, E.N. Durantini, A.L. Moore, D. Gust, and T.A. Moore, "Light-driven Production at ATP Catalyzed by F0F1-ATP Synthase in an Artificial Photosynthetic Membrane," *Nature (London)* **392**, 479–482 (1998).

ACHIEVING DEFECT-TOLERANT AND SELF-REPAIRING SOLAR CONVERSION SYSTEMS

No molecule-based solar energy conversion system, including photosynthesis, or system made from amorphous silicon or many other thin-film inorganic materials, currently maintains its performance in sunlight for 20–30 years. Defect formation mechanisms in photovoltaic materials, as well as self-repair and photo-protection mechanisms in photosynthesis, must be understood and implemented in real-world systems. Achieving defect-tolerant or active self-repair devices would enable the practical utilization of many types of solar energy conversion systems that currently are too unstable to last for the required 20–30 years of operation to produce cost-effective solar electricity or fuels.

EXECUTIVE SUMMARY

Insensitivity of performance to manufacturing and usage-induced defects over a pre-specified range is an inherent requirement of system design, specification, affordability, and performance for extended periods of time in real-world systems. By way of contrast, biological systems, such as photosynthesis, have built-in repair mechanisms that can restore useful function following damage to the system. Identifying and implementing fault-tolerant and/or self-repair paradigms in inorganic and organic systems is a "grand-challenge"-level basic science enterprise that would revolutionize not only the solar energy conversion field but a wide variety of other application areas as well. To ensure that complex systems designed for solar fuels production maintain their efficiency over long lifetimes, the following research directions must be addressed: (1) understand the factors affecting interactions between a large variety of possible structural defects and charge carriers in inorganic PV materials; (2) understand repair and photoprotection mechanisms in natural photosynthesis; (3) control three-dimensional architectures in nanoscale materials to promote redundancy and distributed function as a strategy to tolerate defects; (4) explore assembly-disassembly strategies as a mode of self-repair; and (5) develop active repair molecules that specifically identify and target defects and repair them.

SUMMARY OF RESEARCH DIRECTION

The current highest efficiency (~35%) solar cells are the nearly perfect epitaxially grown compound semiconductor multi-junction structures that collect light across the solar spectrum but are both sensitive to defects and prohibitively expensive to mass-produce. There is thus a critical need to discover, design, and synthesize new materials and structures with solar energy conversion properties that are intrinsically insensitive to defects (point and line defects, grain boundaries, impurity/composition, disorder, morphology, and interface defects) and thus relax the strict requirements on manufacturing of nearly perfect material structures. Since absorption of solar photons and separating the resulting electron-hole pair (usually exciton) is the fundamental basis for conversion to electricity, designing materials and structures that inherently permit reduction of defects or allow charge separation and transport mechanisms tolerant of defects is the fundamental challenge faced in realizing high-performance and affordably manufacturable photovoltaic (PV) solar cells. An example of the defect-reduction approach is the use of selective growth on nanoscale spatial templates, which allows relief of the lattice
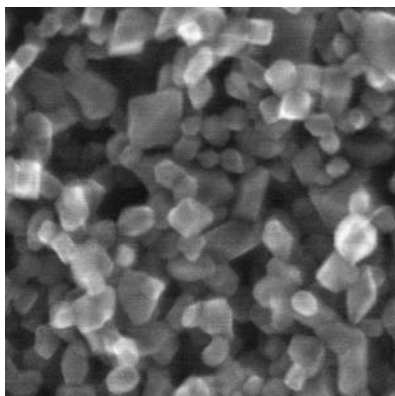
Figure 46 Defect-tolerant solar cell: dye-sensitized solar cell using defective nanoparticulate TiO_2 as electrodes

mismatch strain energy even for highly disparate material combinations, enabling dense arrays of defect-free nanostructures. Alternatively, progress in dye-sensitized nanocrystal-based solar cells provides an excellent example of how a system that tolerates a lack of perfect structural order offers a new, potentially disruptive technology that could have significant impact.

On the other hand, "defect tolerance" in soft materials for photoconversion encompasses two main ideas: self-repair and redundant connectivity. Self-repair can be achieved in several ways: (a) by molecular rearrangement, producing a new defect-free structure because the repaired structure is thermodynamically more stable than a grossly damaged one; (b) using biological structures, including energy-converting structures, swapping out damaged sub-components often (such as molecular chromophores), and replacing them with newly manufactured ones; or (c) leaving damaged components in place and fixing them, rather than replacing or expelling them, such as in enzymatic repair of damaged DNA. "Redundant connectivity" ensures that defects do not disproportionately degrade system performance; it is achieved through multiplicity of equivalent current pathways and is of special importance for nanoscale-material-based solar cells that operate in a current percolation mode. An example is the nanoparticulate photoelectrode of the dye-sensitized nanostructured solar cell — sintering redundantly or multi-dimensionally interconnects particles, as shown in Figure 46.

Within photosynthesis, the most dramatic self-repairing system is the reaction center of Photosystem II (PSII). PSII catalyzes the light-driven splitting of water and involves highly oxidative chemistry. The D1-protein binds the majority of the cofactors involved in light-driven charge transfer reactions of PSII, including the primary electron donor P680 and the Mn-cluster at which the water-splitting reaction occurs. It seems highly likely that the oxidative damage to the D1-protein is due to singlet oxygen and/or oxygen radicals formed during the water-splitting process. The vulnerable D1 protein is removed from the complex from time to time (about 30–60 minutes in an illuminated leaf) and replaced by a newly synthesized D1-protein. Recent biochemical and molecular biological studies are starting to reveal the nature of this process (see Figure 47), yet the molecular details of this remarkable repair mechanism are unknown and are worthy of more intense research.
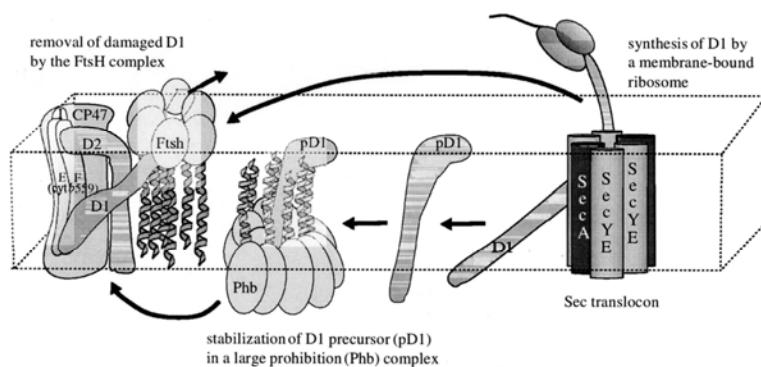

Figure 47 Repair of PSII by degrading photo-damaged D1 protein and replacing it with newly synthesized D1 protein

NEW SCIENTIFIC OPPORTUNITIES

Development of new defect-tolerant inorganic PV materials will require combined experimental and theoretical efforts aimed at understanding the factors affecting interactions between a large variety of possible structural defects and charge carriers. This knowledge could lead to the design and discovery of new classes of materials satisfying the multiple constraints of high-volume, low-cost PV systems, including utilizing abundant elements, environmentally benign chemical components, simplicity of synthesis and processing, and high PV performance efficiency.

Nanoscale building blocks offer many potential advantages for solar energy research, such as the low cost of single-crystal synthesis, the above-noted tolerance for lattice mismatch in heterojunctions, and the ability to control three-dimensional architecture through shape-controlled growth, microphase separation, and layer-by-layer synthesis. Novel architectures such as branched nanocrystals, and templated nanowires and nanotubes provide useful building blocks for coupling of light and photocatalytic components into functioning photocatalytic assemblies. The challenge is to design these assemblies in order to drive energetically demanding reactions, such as water-splitting, by using visible and near-infrared light. It is very important to explore catalysts that are resistant to poisoning.

The challenge of using assembly-disassembly strategies for self-repair is the need to understand the molecular details of how to prepare modular artificial photosynthetic systems. These systems must depend on non-covalent interactions for their assembly and disassembly. The disassembly process must be initiated by recognition of specific damage motifs in the overall artificial photosynthetic system. This requires a design that identifies and anticipates the structural consequences of the principal damage motifs. Once these pathways are identified, the overall molecular recognition properties of each module (which will be based on weak interactions such as hydrogen-bonding, metal-ligand interactions, and/or π-π stacking of chromophores) must be optimized so that a particular module will tolerate only a narrow range of conformations to recognize its partner modules. Deviations from this narrow range of conformations induced by damage in one or more modules will result in spontaneous disassembly driven by thermodynamics. Reassembly with intact modules will be driven by having excess intact modules present in equilibrium with the overall system. This type of approach should work reasonably well for artificial photosynthetic systems immobilized at surfaces, where they could be exposed to a "repair solution" containing the modules needed for replacement.

The most challenging and potentially most general approach to self-repair is the design of smart molecules that will (a) seek out damage sites within a modular artificial photosynthetic system, (b) recognize the damage site, (c) execute a structural repair, and (d) leave the site to seek other damage. This approach requires building into molecules the self-autonomous features that are common in biology, but have not yet been developed for non-living systems.

RELEVANCE AND POTENTIAL IMPACT

Achieving defect-tolerant or active self-repair devices would enable the practical utilization of many types of solar energy conversion systems that are currently too unstable to last for the

required 20–30 years of operation to produce cost-effective solar electricity or fuels. The successful realization of defect-tolerant materials and device structures has the potential to revolutionize the high-volume production of both solar electricity and fuels. The knowledge gained in determining how to actively repair molecular systems will have broad relevance to the vast array of applications that depend on molecular materials.

SOLAR THERMOCHEMICAL FUEL PRODUCTION

Solar concentrating systems currently provide the lowest-cost technology for solar electricity production, and they offer the possibility of economically supplying high-temperature heat for driving thermochemical processes for hydrogen generation. Solar fuel production via thermochemical processes requires fundamental kinetic studies of the reactions involved and the development of novel chemical reactor technology for effecting these high-temperature reactions with high solar-to-fuel energy conversion efficiencies.

RESEARCH DIRECTION

Thermochemical Fuel Production

Research in thermochemical fuel production is aimed at the advancement of the thermochemical and thermo-electrochemical sciences applied to the efficient thermochemical production of solar fuels, with the focus on solar hydrogen production. Concentrated solar radiation is used as the energy source of high-temperature process heat for the endothermic chemical transformations. The research emphasis is on the following areas:

- The fundamental analysis of radiation heat exchange coupled to the kinetics of heterogeneous thermochemical systems;

- The design of advanced chemical reactor concepts based on the direct irradiation of reactants for efficient energy absorption;

- The development of high-temperature materials (T>1,500°C) for thermochemical and thermo-electrochemical reactors; and

- 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.

Hydrogen Production by Solar Thermochemical Processes

Solar Water-Splitting Thermochemical Cycles. The single-step thermal dissociation of water is known as water thermolysis. Although conceptually simple, the direct water-splitting has been impeded by the need for a high-temperature heat source above 3,000K for achieving a reasonable degree of dissociation and by the need for an effective technique for separating H_2 and O_2 to avoid ending up with an explosive mixture. Water-splitting thermochemical cycles bypass the H_2/O_2 separation problem and also allow operating at relatively moderate upper temperatures. Previous studies performed on H_2O-splitting thermochemical cycles were mostly characterized by the use of process heat at temperatures below about 1,200K, available from nuclear and other thermal sources. These cycles required multiple steps (more than two) and suffered from inherent inefficiencies associated with heat transfer and product separation at each step. Status reviews on multistep cycles, with upper temperatures below 1,200K, are given by Funk (2001) and include the leading candidates: General Atomics' three-step cycle based on the thermal decomposition of

H_2SO_4 at 1,130K, and the University of Tokyo Cycle #3 (UT-3) four-step cycle based on the hydrolysis of $CaBr_2$ and $FeBr_2$ at 1,020 and 870K.

In recent years, significant progress has been made in the development of optical systems for large-scale solar concentration; such systems are capable of achieving mean solar concentration ratios exceeding 2,000 suns (1 sun = 1 kW/m^2). Present efforts are aimed at reaching concentrations of 5,000 suns (Steinfeld and Palumbo 2001). Such high radiation fluxes allow the conversion of solar energy to thermal reservoirs at 2,000K and above, which are needed for efficient water-splitting thermochemical cycles using metal oxide redox reactions (Steinfeld 2005). This two-step thermochemical cycle (Figure 48) consists of a first-step solar endothermic dissociation of a metal oxide and a second-step nonsolar exothermic hydrolysis of the metal. The net reaction is $H_2O = H_2 + 0.5O_2$, but since H_2 and O_2 are formed in different steps, the need for high-temperature gas separation is thereby eliminated.
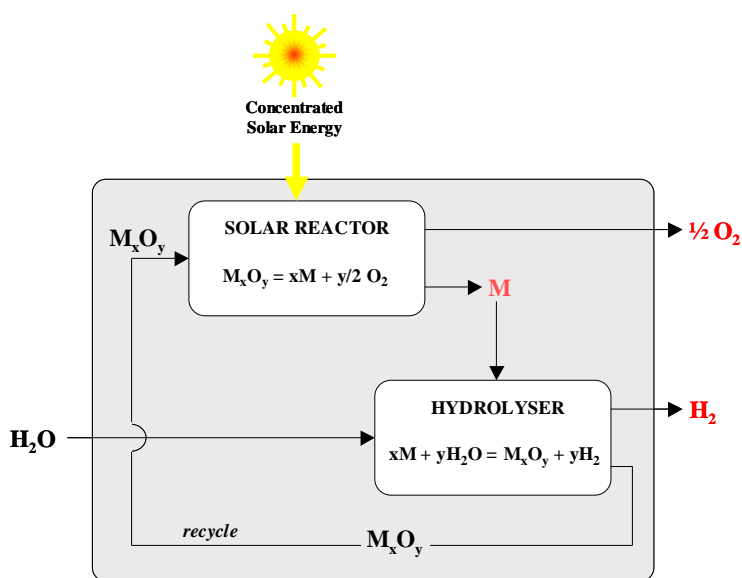

Figure 48 Solar hydrogen production by water-splitting thermochemical cycle via metal oxide redox reactions

This cycle was examined for the redox pairs Fe_3O_4/FeO, Mn_3O_4/MnO, Co_3O_4/CoO, and mixed oxides (Steinfeld 2005 and citations therein). One of the most favorable candidate metal oxide redox pairs is ZnO/Zn. Several chemical aspects of the thermal dissociation of ZnO have been investigated (Palumbo et al. 1998). The theoretical upper limit in the energy efficiency, with complete heat recovery during quenching and hydrolysis, is 58% (Steinfeld 2002). In particular, the quench efficiency is sensitive to the dilution ratio of Zn(g). Alternatively, electrothermal methods for *in situ* separation of Zn(g) and O_2 at high temperatures have been demonstrated (Fletcher 1999); these enable recovery of the sensible and latent heat of the products. Figure 49 shows a schematic of a solar chemical reactor concept that features a windowed rotating cavity-receiver lined with ZnO particles that are held by centrifugal force. With this arrangement, ZnO is directly exposed to high-flux solar irradiation and simultaneously serves the functions of radiant absorber, thermal insulator, and chemical reactant. Solar tests carried out with a 10-kW prototype subjected to a peak solar concentration of 4,000 suns proved the low thermal inertia of

the reactor system — ZnO surface temperature reached 2,000K in 2 seconds — and its resistance to thermal shocks.

Solar Thermal Decarbonization of Fossil Fuels. The complete substitution of fossil fuels by solar hydrogen is a long-term goal. Strategically, it is desirable to consider mid-term goals aiming at the development of hybrid solar/fossil endothermic processes, in which fossil fuels are used exclusively as the chemical source for H_2 production and concentrated solar radiation is used exclusively as the energy source of process heat. The products of these hybrid processes are cleaner fuels than their feedstock because their energy content has been upgraded by the solar input in an amount equal to the enthalpy change of the reaction. The mix of fossil fuels and solar energy creates a link between today's fossil-fuel-based technology and tomorrow's solar chemical technology. It also builds bridges between present and future energy economies because of the potential of solar energy to become a viable economic path once the cost of energy will account for the environmental externalities from burning fossil fuels, such as the cost of greenhouse gas mitigation and pollution abatement. The transition from fossil fuels to solar fuels can occur smoothly, and the lead time for transferring important solar technology to industry can be reduced. Hybrid solar/fossil processes offer a viable route for fossil fuel decarbonization and CO_2 avoidance, and further create a transition path toward solar hydrogen.

Three thermochemical processes are considered: (1) solar thermal decomposition, (2) steam reforming, and (3) steam
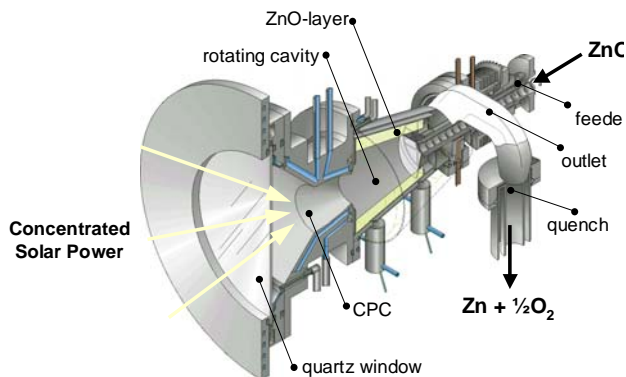

Figure 49 Schematic of a solar chemical reactor for the thermal dissociation of ZnO to Zn(g) and O_2 at above 2000K, as part of a two-step water-splitting thermochemical cycle (Steinfeld and Palumbo 2001)
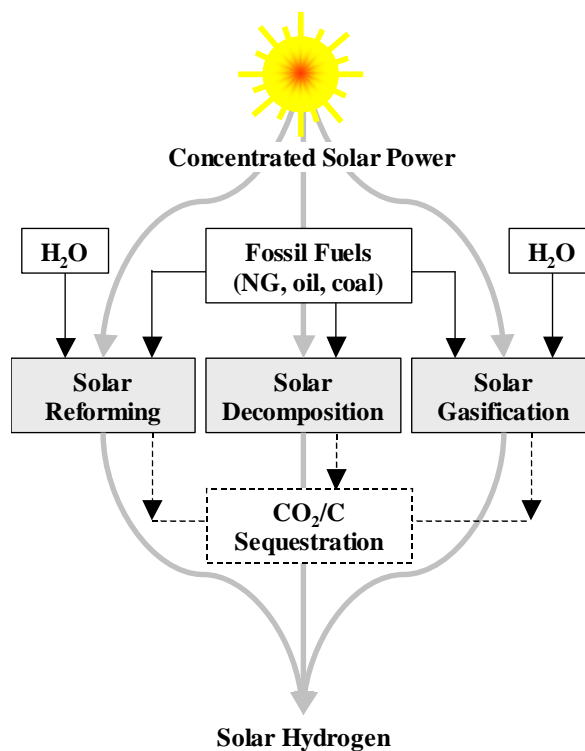

Figure 50 Scheme of three hybrid solar thermochemical routes for the production of hydrogen by thermal decarbonization of fossil fuels: solar decomposition, solar reforming, and solar gasification

gasification. These processes, depicted in Figure 50, make use of high-temperature solar heat for driving the endothermic transformations. Since the reactants contain carbon, an optional C/CO_2 sequestration step is added to the scheme for CO_2-free production of H_2. However, even without

the sequestration step, these solar-driven processes offer significant reduction in CO_2 emissions compared with conventional combustion-based processes. A Second-Law analysis for generating electricity indicates the potential of doubling the specific electrical output and, consequently, halving the specific CO_2 emissions compared with conventional fossil-fuel power plants (von Zedtwitz and Steinfeld 2003). These processes proceed endothermically in the 800–1,500K range. The advantages of supplying solar energy for process heat are threefold: (1) the calorific value of the feedstock is upgraded by adding solar energy in an amount equal to the enthalpy change of the reaction; (2) the gaseous products are not contaminated by any combustion by-products; and (3) the discharge of pollutants to the environment is avoided. The solar chemical reactor technology for these processes includes a vortex-type and an aerosol-type flow reactor for solar natural gas decomposition (Hirsch and Steinfeld 2004; Dahl et al. 2004; Kogan et al. 2005), a catalytic porous-ceramic absorber for NG reforming (Moeller et al. 2002), and a fluidized bed reactor for coal gasification (Müller et al. 2003; Trommer et al. 2005). The experimental demonstration of solar reactor prototypes points toward developing solar chemical technology to an industrial megawatt scale.

SCIENTIFIC CHALLENGES

Radiative Exchange In Chemically Reacting Flows

Fundamental research, both theoretical and experimental, is 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/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°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 stable

structural materials at T>800°C and materials that can be used for various components of the solar reactor and electrolysis units, such as absorbers, electrolytes, and electrodes.

RELEVANCE AND POTENTIAL IMPACT

This research will lead to the efficient and cost-effective industrial production of solar hydrogen and other solar chemical fuels.

REFERENCES

J. Dahl et al., "Solar-thermal Dissociation of Methane in a Fluid-wall Aerosol Flow Reactor," *Int. J. Hydrogen Energy* **29**, 725–736 (2004).

E.A. Fletcher, "Solar Thermal and Solar Quasi-electrolytic Processing and Separations: Zinc from Zinc Oxide as an Example," *Ind. Eng. Chem. Res*. **38**, 2275–2282 (1999).

J. Funk, "Thermochemical Hydrogen Production: Past and Present," *Int. J. Hydrogen Energy* **26**, 185–190 (2001).

D. Hirsch and A. Steinfeld, "Solar Hydrogen Production by Thermal Decomposition of Natural Gas Using a Vortex-flow Reactor," *Int. J. Hydrogen Energy* **29**, 47–55 (2004).

A. Kogan, M. Kogan, and S. Barak, "Production of Hydrogen and Carbon by Solar Thermal Methane Splitting – III. Fluidization, Entrainment and Seeding Powder Particles into a Volumetric Solar Receiver," *Int. J. Hydrogen Energy* **30**, 35–43 (2005).

S. Moeller et al., "Solar Production of Syngas for Electricity Generation: SOLSYS Project Test-phase," *Proc. 11th SolarPACES Int. Symp*., Zurich, Switzerland, pp. 231–237 (2002).

R. Müller et al., "Kinetic Investigation on Steam Gasification of Charcoal under Direct High Flux Irradiation," *Chem. Eng. Sci*. **58**, 5111–5119 (2003).

R. Palumbo et al., "The Production of Zn from ZnO in a Single Step High Temperature Solar Decomposition Process," *Chem. Eng. Sci*. **53**, 2503–2518 (1998).

A. Steinfeld and R. Palumbo, "Solar Thermochemical Process Technology," in *Encyclopedia of Physical Science and Technology*, R.A. Meyers (Ed.), Academic Press, **15**, 237–256 (2001).

A. Steinfeld, "Solar Hydrogen Production via a 2-step Water-splitting Thermochemical Cycle based on Zn/ZnO Redox Reactions," *Int. J. Hydrogen Energy* **27**, 611–619 (2002).

A. Steinfeld, "Solar Thermochemical Production of Hydrogen — A Review," *Solar Energy* **78**(5), 603–615 (2005).

P. von Zedtwitz and A. Steinfeld, "The Solar Thermal Gasification of Coal — Energy Conversion Efficiency and CO_2 Mitigation Potential," *Energy - The International Journal* **28**(5), 441–456 (2003).

D. Trommer et al., "Hydrogen Production by Steam-gasification of Petroleum Coke Using Concentrated Solar Power — I. Thermodynamic and Kinetic Analyses," *Int. J. Hydrogen Energy* **30**, 605–618 (2005).

NEW EXPERIMENTAL AND THEORETICAL TOOLS TO ENABLE TRANSFORMATIONAL RESEARCH

Solar energy conversion systems involve many components to achieve the functions of light capture, conversion, and storage. Experimental tools and theoretical capabilities that can capture the behavior of these systems, which span many decades in space, time, and structure, do not yet exist. Development of such tools would allow experimentalists to directly probe the behavior of molecules, materials, structures and devices, and could enable the theoretical prediction of optimally performing structures without having to first make the systems in the laboratory.

EXPERIMENTAL TOOLS: REAL-TIME LOCAL PROBES FOR ATOMISTIC STRUCTURE AND FUNCTION

Overview

Efficient conversion of solar energy to electricity and chemical fuels requires complex interplay between multiple functional components and processes occurring in differing length and time scales. Consider, for example, a Grätzel cell where photoexcited redox reactions on nanostructured titania (TiO_2) are used to generate electricity. The operation of the Graetzel cell involves the efficient photon absorption by organic dye molecules, separation of an electron and a hole at the molecule-TiO_2 interface, electron transport through TiO_2 grain boundaries, energy relaxation and charge trapping, solution phase electrochemistry, and the mass transport through the electrolyte solution. Essentially all known solar energy conversion processes involve similarly complex physical and chemical processes intertwined with each other, and the efficiencies and fidelity of solar energy conversion depend critically on the atomistic detail of the molecule and material systems involved.

The design and optimization of an effective solar energy conversion system requires experimental tools for investigating these complex, multi-scale processes and their interplay at the system-wide level. Despite the spectacular expansion of experimental tools that has occurred over the last several decades, none of the existing techniques allows a detailed atomistic investigation of these complex processes in real time, pointing to the need for new, transformative experimental tools in solar energy research.

Research Needs

In principle, an ideal experimental tool should be able to monitor physical and chemical processes on the full range of length and time scales involving electronic, molecular, nanoscale, and macroscopic degrees of freedom. This is a daunting challenge, and experimental tools with the potential to address this complex multi-scale problem are only beginning to emerge (see Figure 51). Electron microscopy and X-ray/neutron diffraction techniques have enabled the detailed interrogation of bulk, interfacial, and nanoscale structures with atomic resolution, and can be used for structural investigation of various components in solar energy conversion systems.

The continued advances in energy- and time-resolved spectroscopy have allowed the detailed interrogation of photoinitiated molecular processes in real time, and provided insight into molecular and chemical processes in photoelectrochemical and catalytic systems. The advent of scanned probe microscopy has enabled, on the other hand, both structural and functional imaging of various physical processes with near-atomic precision. These tools, combined with advances in nanofabrication techniques, have allowed the direct visualization of charge transport and charge trapping in nanoscale systems, and provided functional snapshots of critical events in photovoltaic devices.

Continued and vigorous efforts to develop and extend these experimental tools are essential for solar energy research. Prominent examples that need to be developed further include X-ray and transmission-electron-microscope tomography, which will allow the determination of three-dimensional structure of individual nanostructures with atomic precision. Nanoscale components play important roles in many solar energy conversion systems, including organic and hybrid photovoltaic cells,

Figure 51 Emerging experimental tools: (a) scanned gate (left) and electrostatic force (right) microscopy images of individual nanostructures that allow the combined structural and functional characterization of individual defects; (b) schematic diagram of X-ray nanoprobe (ANL) that will allow the structural characterization of nanoscale structures.

photoelectrochemical cells, and photocatalytic fuel generation; the new capability afforded by atomic resolution tomography will facilitate the design and characterization of nanostructures with improved functionalities.

Another important experimental tool that is currently lacking is scanned probe techniques with chemical specificity. In many photoelectrochemical and catalytic systems, the chemical processes that occur at electrode-solution interface play a quintessential role. Scanned "chemical-probe" microscopy should allow the discrimination of distinct chemical species in complex environments and hence, the monitoring of interfacial chemical reactions with nanoscale resolution. The knowledge gained in these studies should then provide detailed new insight into characterizing and optimizing solar fuel systems, an important ingredient of a viable solar energy future.

In addition to developing experimental tools with new capabilities, significant efforts should also be directed toward integrating functionalities of distinct experimental tools to enable simultaneous structural and functional imaging of solar energy conversion systems with requisite time resolution. This integration effort is all the more critical because most current experimental tools are limited to the characterization of individual components and processes and fail to provide system-wide insight into the structure and function of solar energy conversion systems.
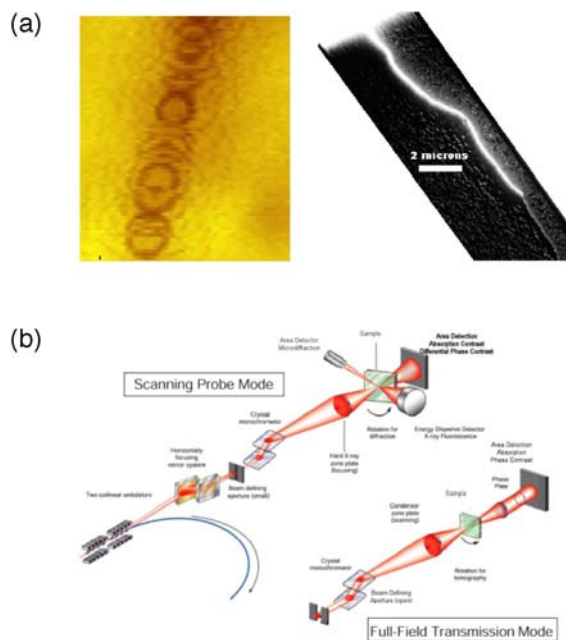
Important examples include a combination of ultrafast lasers, scanned probe/near-field microscopy, and transport measurements; this combination should (1) allow the integrative real-time interrogation of photoabsorption and charge separation/transport with near-atomic precision and (2) enable the investigation of the most important step in solar energy conversion processes in unprecedented detail. The knowledge obtained in this type of study will revolutionize the knowledge base necessary for optimizing existing and future solar energy conversion systems. The combination of ultrafast laser with X-ray and neutron absorption/scattering/diffraction techniques (both table-top and large facilities) (see Figure 52) should enable, on the other hand, *in-situ* structural resolution of molecular and material dynamics across the multiple time and length scales, and will provide critical insight into both photocatalytic and photosynthetic processes.

Figure 52 New experimental tools that allow the combined structural and functional characterization of solar energy conversion systems. (a) Scanned photocurrent (left) and electroluminescence measurements of individual nanostructures. (b) Combined ultrafast laser and X-ray measurements of photochemical systems.

Impact

The new experimental tools mentioned above and the capabilities afforded by them will play an essential role in characterizing photovoltaic, photoelectrochemical, and solar fuel systems. The knowledge gained from these studies will, in turn, enable the critical assessment and optimization of the performance characteristics of existing strategies of solar energy conversion. Furthermore, together with new theoretical and computational tools, the new techniques will help to test and confirm the operation of potentially revolutionary solar energy conversion devices and will thereby facilitate the development of disruptive new solar energy conversion strategies.

CROSS-CUTTING THEORETICAL TOOLS

Overview

Good candidate systems for effective solar energy utilization are based on physical and chemical processes occurring on the full range of length and time scales from the electronic atomic to the macroscopic. Solar energy systems exploit complex phenomena, molecules, and materials, and their interplay with the system architecture. These two cross-cutting basic scientific themes — complexity and multi-scale phenomena — make imperative the continual intimate interaction of experiment and theory, for which new theoretical tools are required to guide and interpret experiment and assist in the design of molecules, materials, and systems. A further precondition
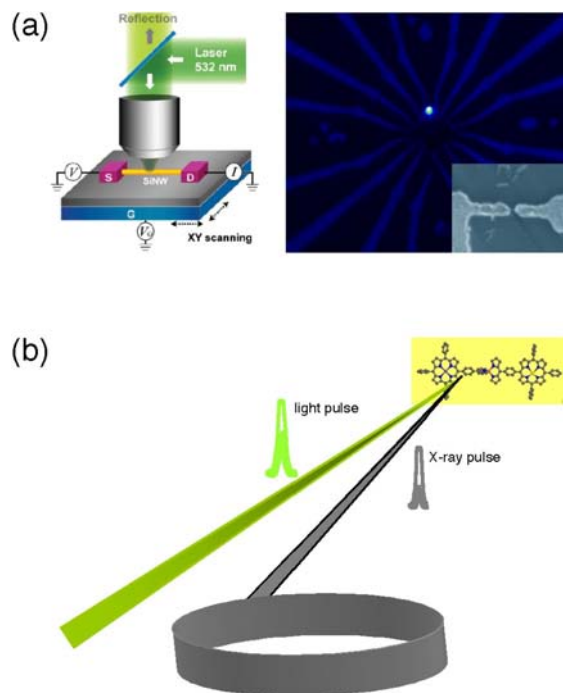
for the detailed understanding and optimization of these systems is a set of complementary advances in experimental techniques for structural and functional characterization from the atomic to the macroscopic in time and space, with continual interplay between experiment and theory.

Research Needs

New theoretical, modeling, and computational tools are required to meet the challenges of solar energy research. Currently, highly accurate quantum mechanical schemes, based on density functional theory (see Figure 53), are well established to describe ground state structures of systems consisting of up to a few hundreds of atoms. In order to successfully describe the processes that are relevant to solar energy conversion, the capability of these approaches will need to be enhanced to deal with thousands of atoms: this will require the practical implementation of novel linear scaling methodologies. In addition, methods for excited-state potential energy surfaces will have to be developed and tested. Alternative approaches to deal with excited-state properties are based on time-dependent density functional theory, on many-body perturbation theory, and on quasi-particle equations, but a consensus on their accuracy is not broadly available yet, nor have these approaches been applied to systems with the complexity of the nanoscale components of solar energy conversion devices. Better schemes for excited states also will be useful to accurately predict band-gaps and band gap line-ups in a variety of solar energy systems.
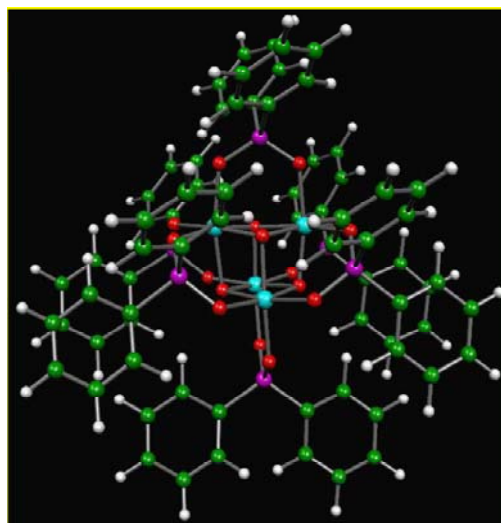

Figure 53 Density functional theory calculations give the optimized geometry of a $(Ph_2PO_2)_6Mn_4O_4$ cubane complex (a quasi-cubane Mn cluster) that is relevant to photosynthesis.

Solar energy conversion processes, such as the processes that lead to photosynthesis, are characterized by activated catalytic processes, which cannot be simulated on the short time scale of molecular dynamics simulations. In this case, approaches like first-principles molecular dynamics, which use a potential energy surface generated from ground-state density functional theory, need to be supplemented by approaches for finding chemical reaction pathways both at zero and at finite temperature. These approaches should allow us to characterize the reaction intermediates and transition states in chemical and photochemical reactions in processes like water-splitting, which is essential to solar hydrogen production by hydrolysis. *Ab initio* quantum mechanical methods will need to be extended to deal with up to tens of thousands of atoms, by means of parameterized empirical or semi-empirical approaches. To understand the complex organization and assembly of biological light harvesting systems that are made of non-covalently bonded molecular subunits, classical force fields are required: these will need improved formulations for dispersion forces. Finally, charge and energy transfer, trapping, and recombination/relaxation processes are crucial in all energy conversion devices from photovoltaic, to photoelectrochemical, to natural (biological) systems. Modeling these processes

will require significant new progress even at the level of basic theory, let alone computational algorithms and their numerical implementation. For instance, successful modeling will require effective schemes for non-adiabatic quantum molecular dynamics and schemes for quantum transport in the presence of dissipative processes and/or in disordered media.

Strong interaction between experiment and theory will be essential to develop the new theoretical tools: experiment will guide theory to identify basic physical processes and to validate the theoretical tools. Theory, in turn, will guide the interpretation of experiment and provide detailed models for energy conversion processes. When, for a given system, understanding proceeds to the point where specifications of the goals for material properties and system performance can be made with some confidence, the computational procedure can be reversed, that is, formulated as an inverse problem. In this approach, theory can be used to design by computer a material composition and structure (see Figure 54), a system architecture, or a process dynamic that meets a set of desired specifications.

Figure 54 Self-assembled structure generated by computer simulation

The above-described program requires large-scale computations, which will need access to adequate computational facilities, including super and ultra computer facilities.

Impact

The ability to carry out such multiscale computation, the models generated thereby and the effective interaction with experiment thus made possible would profoundly enhance our insight into the functioning of all the systems covered in the workshop as well as those to emerge in the future. It would enable the design of improved devices, both by the elucidation of existing and currently proposed systems and by direct suggestion of alternatives. It would enhance the effectiveness and the efficiency of the coordinated experimental programs. Progress toward the goals of the workshop — the creation of the basic energy science needed for the effective utilization of solar energy as heat, electricity, or fuel — would be substantially accelerated across all areas.
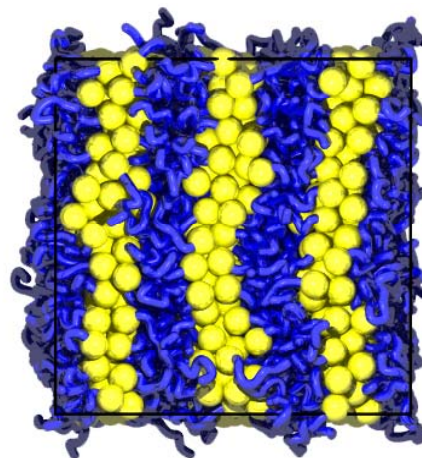
SOLAR ENERGY CONVERSION MATERIALS BY DESIGN

Materials play a key role in various aspects of solar energy conversion. Presently available materials are generally deficient in performance, cost, stability, or some combination thereof. New materials systems, guided by the interplay between rational design, high-throughput screening, and theory, are needed to improve the performance of light absorbers, photovoltaic materials and photoelectrodes, catalysts, thermoelectrics, and infrastructural aspects of solar energy conversion systems.

EXECUTIVE SUMMARY

Materials play a key role in solar energy conversion to electricity, fuels, and heat. Materials used in photovoltaics have traditionally been derived from research and development advances in other technology fields (e.g., Si from microelectronics industry, GaAs from optoelectronics industry), and as a result, the range of materials currently available for use in photovoltaics is highly limited compared to the enormous number of semiconductor materials that can in principle be synthesized for use in photovoltaics. Similarly, high-efficiency thermoelectric and thermophotovoltaic converters coupled to solar concentrators have the potential to generate electricity at converter efficiencies from 25 to 35%. Significant progress has been made in these areas over the last decade, particularly by exploiting nanoscience and nanotechnology. Further fundamental research can lead to cost-effective materials that enable efficient solar-thermal energy utilization systems, by developing thermoelectric materials with ZT up to 4, selective thermal emitters that can withstand >1,000°C, high thermal conductivity polymer-based materials, and new photovoltaic absorbers and transparent conductors. In order to identify materials that are ideally suited to solar energy conversion and storage applications, new experimental and theoretical methods are required that can rapidly assess and select promising materials from a very large number of candidates. Moreover, the materials selection principle should be the desire to first optimize a particular material property for use in a device, and subsequently search among all possible materials for a few specific candidates based on property-driven selection criteria. Thus, both experimental methods for high-throughput screening of materials and theoretical methods that identify electronic and atomic structure based on targeted material properties are needed. Solar concentrators and hot water heaters call for new low-cost polymer-based materials/composites, while new solar thermal storage materials are required for several solar thermal conversion applications.

RESEARCH DIRECTIONS

Solar Photon Converters

The traditional approach to development of new materials for application in photovoltaics has been to identify materials developed for other technological purposes and assess their suitability to adaptation in photovoltaics. Thus, the materials themselves were developed for other purposes, and their development often follows the basic sequence in which (1) an interesting property is discovered; (2) a useful application is invented; (3) "basic research" starts; and (4) development occurs until the material is of adequate quality for the identified application.

A shortcoming of this approach is that the discovery process relies on accident or serendipity, or targeting in a limited domain, and ultimate success requires a long research and development process. A more desirable approach (Franceschetti and Zunger 1999) is one that emphasizes design of materials with targeted properties as an integral part of the discovery process (see Figure 55). New approaches to discovery-by-design can be based on several observations:

- Current research-oriented advanced materials synthesis and processing methods can produce a wide variety of both equilibrium and nonequilibrium atomic configurations — almost at will.

- The choice of atomic configuration in a material controls many of its physical properties.

- There are often too many possible atomic configurations for direct and explicit prediction of properties.

Thus, the challenge underlying these observations is to identify an atomic configuration (structure) with a given, useful target property, out of an astronomical number of possibilities (Franceschetti and Zunger 1999). Progress in both theoretical and experimental methods is needed. For photovoltaics and photoelectrodes, the materials properties that need to be identified and optimized include semiconductor band structure, band gap, band edge energies, carrier mobilities, electron affinity, work function, oscillator strength and selection rules (direct vs indirect band gap), phonon spectrum, electron-phonon scattering parameters, lattice constants, atomic order-disorder behavior, and defect structure. The specific properties required will depend upon the specific type of device being considered.
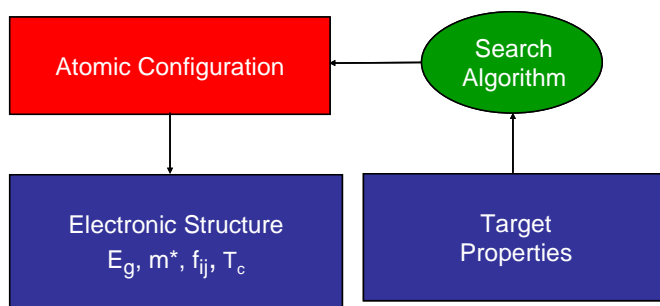

Figure 55 Materials by design. In one manifestation, the process begins with a set of target properties. A simulation tool is combined with a search algorithm process to find a test atomic configuration, then calculates the values of the properties and adjusts the configuration if necessary. The loop is repeated until the calculated properties match the target input.

Thermoelectrics

Comprehensive Theoretical Guidance on Thermal and Electronic Transport in Complex Structures. Over the past decade, progress has been made in the theory of thermoelectricity, noticeably the work of quantum size effects on the electronic power factor (Hicks and Dresselhaus 1993), interface effects on the thermal conductivity (Chen 2001; Chen et al. 2003), and the use of density functional theory for the electron and phonon band structures (Singh 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 materials with high values of ZT, the thermoelectric figure of merit.

New, High-performance Bulk Materials. Several new bulk materials that exceeded ZT of 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 exhibited 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 (see Figure 56). Developing synthetic processes to fabricate controlled nanoscale substructures is an important undertaking.

Nanoscale thermoelectric materials that can independently reduce phonon transport without deteriorating electronic transport have been implemented in Bi_2Te_3/Sb_2Te_3 superlattices (Venkatasubramanian et al. 2001) offering a ZT
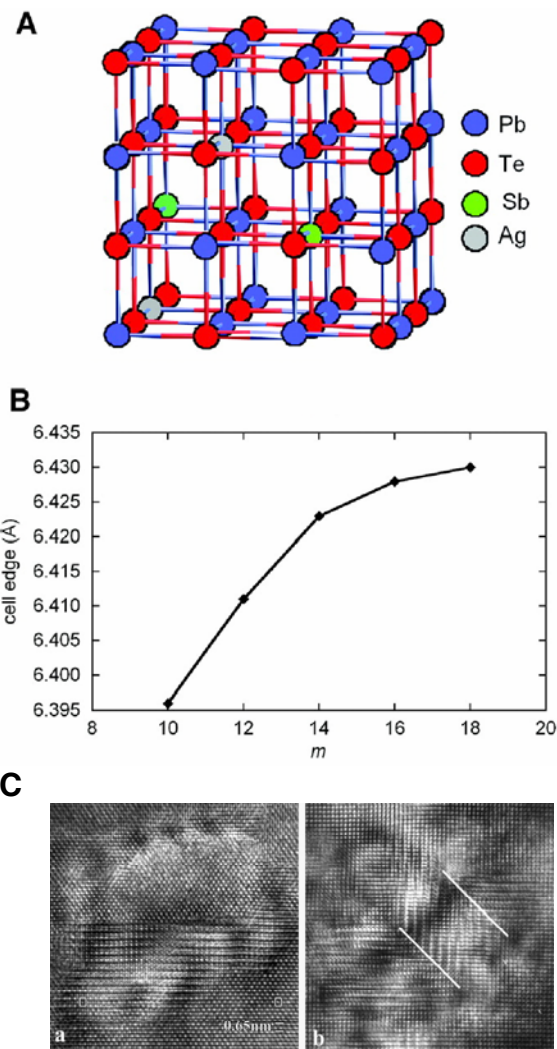

Figure 56 The difficulty of searching experimentally for the optimal high-ZT material is illustrated in this figure. AgPbmMTe2+m (where M is either Sb or Bi and m varies from 10 to 18) is a candidate for a high ZT material. What is the optimal composition? Fig. 56A shows the average ideal crystal structure; repeated x-ray diffraction experiments indicate that the lattice constant varies with m for M=Sb, as shown in Fig. 56B. But TEM reveals that the x-ray diffraction has not detected the presence of nanodots of differing composition in Fig. 56C. (Courtesy of M. Kanatzidis)

of ~2.4 at 300K and quantum-dot PbTe/PbTeSe superlattices (Harman et al. 2002) offering a ZT of ~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 the TPV cells (Coutts et al. 2003). The efficiency of TPV systems depends critically on the 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, the temperature of the emitters exceeding 1,000°C imposes great challenges to the stability of the materials and structures used in a TPV system, especially for those components that provide spectral control.

Solar Concentrators and Hot Water Heaters

Today's concentrators generally consist of a precise shaped metallic support structure and silver-glass reflector elements with an average reflectivity of 88%. They are responsible for more than 50% of the investment costs 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/glass components to integrated systems manufactured using mass production technique, such as those associated with polymeric materials. Major limitations of currently availably polymers are outdoor durability (UV; water, oxygen, mechanical stress, thermal stress) for at least 20 years. Needs include development of thin-film protection layers for reflectors, high strength, high thermal conductivity polymers; development of materials with high transparency and durable glazing for heat exchangers, and engineered surfaces that prevent dust deposition on reflector surfaces.

Thermal Storage Materials

Innovative thermal storage methods must address the need to provide reliable electricity supply based on demand, which generally does not coincide with the incident sunlight periods, as demonstrated in Figure 57. Achieving this requires the development of high energy density, high thermal conductivity, and stable, latent heat materials for thermal storage. One promising approach is using encapsulated and nanocrystal polymers.

The operating conditions (i.e., temperature and pressure) of the thermal storage must match those of the power conversion process, and therefore, vary from 80–150°C for low-temperature systems and 400–1,000°C for high-temperature systems. Solar-derived fuels become the logical choice for storage at >1,000°C.
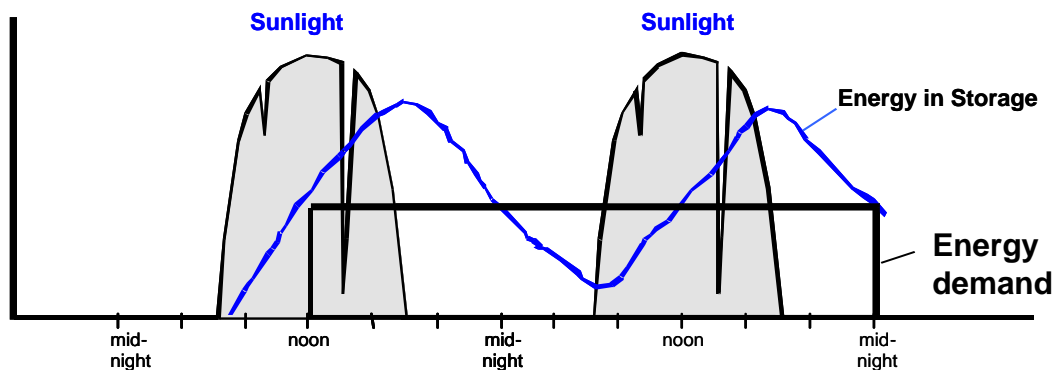
Figure 57 Example of the periodic variation of incident sunlight and thermal energy in the storage, relative to energy demand

SCIENTIFIC CHALLENGE

Theoretical Methods to Identify Photovoltaic Materials with Targeted Properties

Currently, theoretical tools exist that enable first-principles calculation of total-energy and ground state electronic structure (e.g., density functional theory), but such methods are computationally very expensive. Even more expensive is accurate calculation of electronic excited states using, for example, quantum Monte Carlo methods. Thus, first-principles theoretical treatment of systems with many more than 1,000 atoms is currently beyond practicality for most systems. Thus it is not practical to use first-principles methods to exhaustively calculate the atomic and electronic structure of all possible photovoltaic materials. Methods that could circumvent this limit would be those that enable property-based identification of promising candidate materials and then subsequently calculate electronic structure of a restricted set of chosen materials (see Figure 58). Methods to select candidates might include cluster variation-based methods and simulated annealing, genetic algorithms, among others (Franceschetti and Zunger 1999).
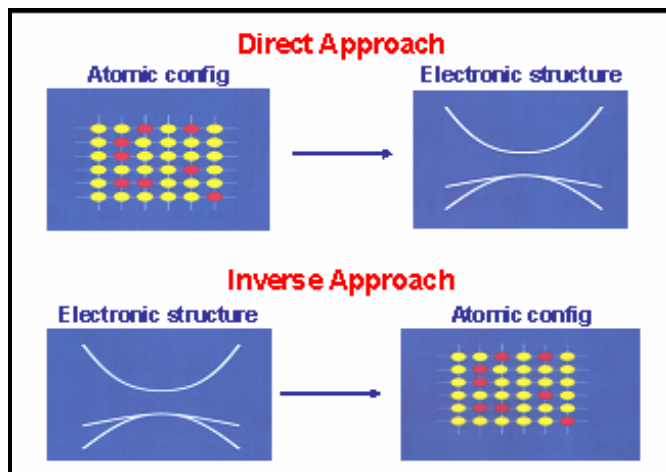

Figure 58 Inverse electronic structure calculations. In the direct approach, the modeler starts with a given atomic configuration and calculates the electronic structure. In the inverse approach, the modeler is told the electronic structure and must search to find an atomic configuration that will produce an electronic structure close to the one required. The inverse approach is a more difficult challenge.

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High-throughput Experimental Screening Methods for Discovery of Designed Materials

Determining the suitability of materials for photovoltaics is currently not a systematic process. For example, one of the most widely used semiconductors for thin-film photovoltaic cells is copper-indium/gallium-diselenide ($Cu_xGa_{1-x}InSe_2$). It was unexpectedly discovered that small-area $Cu_xGa_{1-x}InSe_2$ cells work very well, despite being polycrystalline and containing many point defects, because sodium diffuses from glass substrates into the $Cu_xGa_{1-x}InSe_2$ film, interacts with grain boundaries, and reduces recombination. Had the initially undesired sodium diffusion not occurred, it is not clear that $Cu_xGa_{1-x}InSe_2$ technology would have reached its current state of development. This example points out the importance of experimentally testing films with many combinations of elements, even if there is no underlying heuristic or formal theoretical prediction suggesting that such combinations might have desirable properties. Since there are enormous numbers of alloy compositions to try, high-throughput screening methods are needed. Furthermore, promising polycrystalline thin-film solar cells based on CdTe and $CuInSe_2$ are dramatically affected by the grain structure resulting from growth on foreign substrates, intentional and/or unintentional doping by impurities, the nature of the active junction, and ohmic contacts; all these processes and effects are poorly understood. A basic understanding of these issues would facilitate a revolutionary advance in the performance and economic viability of polycrystalline thin-film PV.

A big research challenge here is to find appropriate and efficient tests of specific photovoltaic properties that enable testing for millions of material combinations. Materials synthesis is often not itself the bottleneck in an approach, owing to relatively straightforward vapor deposition methods for multiple source deposition of elements to form compounds; the more difficult challenge is often to develop experimental methods for properties-based materials selection. As an example, the energy band gap of the materials could quickly be determined by measuring the absorption spectrum. Some information on the rate at which recombination occurs could be determined by measuring the photoluminescence efficiency. Conceivably, arrays of solar cells could be made to directly determine quantum efficiency, fill factor, and open circuit voltage; in this case, contact-less methods for properties measurements would be highly desirable. Pump-probe spectroscopic techniques could be used to determine the cross-section for impact ionization (multiple electron-hole pair generation). Ideally, such screening methods will identify good candidates for more thorough photovoltaic testing.

Thermoelectrics

Fundamental Understanding of Nanoscaled Inclusions in Bulk Materials. Nanoengineered bulk materials may indeed be a key to achieving high-performance bulk thermoelectric materials. Understanding the role and stability of the interface between the nanomaterials and the matrix is essential in order to effectively optimize the materials. An effective interface must be thermally stable and promote electron transport while impeding phonon transport. Interface issues such as diffusion and segregation processes, doping and composition of the nanostructures, differential thermal expansion, and chemical contrast are essential for investigation.

Role of Interfaces in Nanocomposite Materials. Experimentally obtained improvements in ZT in two superlattice structures benefited mainly from reductions on the phonon thermal conductivity. A further increase in ZT in a wide range of structures and materials is possible by engineering phonon transport through interfaces. For example, it has been demonstrated experimentally that the phonon thermal conductivity of superlattices can be significantly smaller than the theoretical minima of their constituent bulk materials (Costescu et al. 2004). Modeling suggests that it is the incoherent superposition of interface reflection of phonons that is the major cause of phonon thermal conductivity reduction (Chen 2001; Chen et al. 2003). However, phonon reflection and transmissivity at single interfaces cannot be predicted at this stage, except at very low temperatures.

Electron Transport in Nanoscale Materials. While there has been significant attention paid to phonon transport in nanoscale systems, only a limited study of electronic transport in nanoscale thermoelectric materials and structures has been conducted. Significant opportunities exist for fine-tuning in two-dimensional superlattices to optimize the mini-band conduction as well as obtain a delta function in DOS. A major development in itself could be the general theory of electronic transport in solid state materials, with ZT >1, where isothermal conditions cannot be assumed during current flow. A new theoretical framework needs to be developed in the study of solid-state thermoelectrics, where quantum effects, multi-valley effects, strain-induced band-gap engineering effects, sharp DOS, and nonisothermal electronic transport are all brought into play. Theoretical and experimental methodologies to determine these quantities should be developed.

Thermophotovoltaics

We need to gain a basic understanding of novel materials for spectral control (Fleming et al. 2002; Greffet et al. 2002). Photonic crystals, plasmonics, phonon-polaritons, coherent thermal emission, left-handed materials, and doping with lanthanides are concepts from the optics community that can be exploited for the spectral control components required in TPV systems. Insight has to be gained into fundamental processes, such as emission.

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 ~1,200°C in fuel-powered TPV and ~2,000°C in solar TPV. Diffusion processes and evaporation of material may limit the durability of the components significantly. Suitable concepts of material engineering to reduce theses 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. The techniques for producing nanostructures are top-down approaches that are limited to small, homogeneously structured areas and to flat surfaces nowadays. They are also not cost-efficient. Thus, novel techniques have to be developed, which very likely incorporate self-organization processes.

Solar Concentrators and Hot Water Heaters

Heat transfer surfaces for water heaters call for polymer/composites with high mechanical strength, UV degradation resistance, high thermal conductivity, and concentrator support structures requiring polymers with high mechanical strength and a low thermal expansion coefficient. The thermal conductivity of most polymers is 0.2 to 0.4 W/m-K. An order-of-magnitude 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 explore the concept of photonic crystals. Mirrors and glass that are dirt repelling 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.

Thermal Storage Materials

Fundamental understanding of the behavior of phase change storage materials (PCM) and the relationship between various (sometimes undesirable) chemical processes, phase transition, and thermal/chemical stability are crucial for the development of thermal storage. These materials 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 of nanocrytstal polymer composites can be the key to 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 thermal storage 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 (see Figure 59). Further, a nanocrystal can change shape and volume without undergoing fracture or plastic deformation. In addition, the barrier to a structural transition depends strongly on the size of the nanocrystals so that 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 degrees Celsius), so exploratory work must be performed to find materials and transitions that will perform thermal storage under the appropriate conditions for solar thermal.
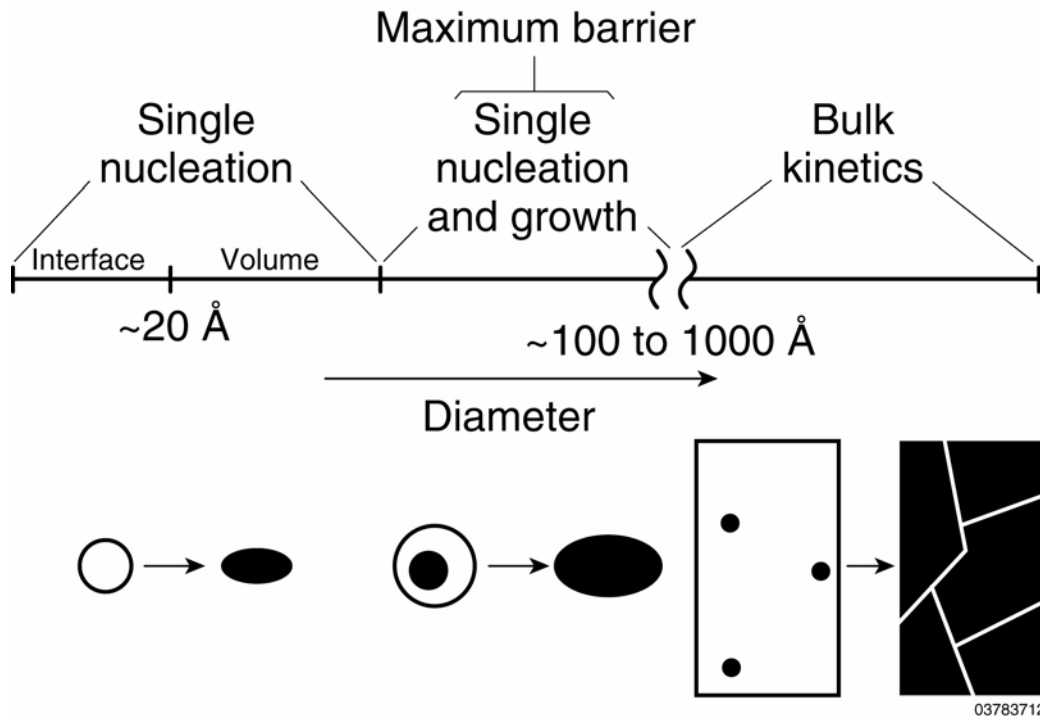
Figure 59 Illustration of various size regimes of the kinetics of solid-solid phase transitions. Defects, which act as nucleation sites, are indicated by asterisks in the cartoon of the bulk solid.

POTENTIAL IMPACT

An R&D investment in basic science and technology targeting solar-related materials is extremely relevant to the efficiency and cost goals of DOE in the solar area. Although there are several materials available to make thin-film PV cells today, an ideal material has not yet been found. Experimental and theoretical screening could discover several direct band-gap semiconductors that have band-gaps ranging from 0.7 eV to 2.5 eV, function well in PV cells, and are made from elements abundant in the Earth's crust. New materials could lead to the development of devices that enable the achievement of a ~35%-efficient power conversion in concentrated solar systems. Successful research on new polymer materials can lead to a 15% efficiency improvement and a factor of two reduction in cost, which would represent a revolutionary breakthrough in solar thermal electricity and space heating. New effective thermal storage materials and systems will be a great advance towards dealing with the issues of diurnal solar energy.

REFERENCES

G. Chen, "Phonon Heat Conduction in Low-Dimensional Structures," *Semicond. & Semimetals* **71**, 203–259 (2001).

G. Chen, M.S. Dresselhaus, J.-P. Fleurial, and T. Caillat, "Recent Developments in Thermoelectric Materials," *Int. Mat. Rev.* **48**, 45–66 (2003).

R.M. Costescu, D.G. Cahill, F.H. Fabreguette, Z.A. Sechrist, and S.M. George, "Ultra-low Thermal Conductivity in W/Al2O3 Nanolaminates," *Science* **303**, 989–990 (2004).

T.J. Coutts, G. Guazzoni, and J. Luther, "An Overview of the Fifth Conference on Thermophotovoltaic Generation of Electricity," *Semicond. Sci. Technol.* **18**, S144–S150 (2003).

J.G. Fleming, S.Y. Lin, I. El-Kady, R. Biswas, and K.M. Ho, "All Metallic Three-dimensional Photonic Crystals with a Large Infrared Bandgap," *Nature* **417**, 52–55 (2002).

A. Franceschetti and A. Zunger, "The Inverse Band Structure Problem: Find the Atomic Configuration with Given Electronic Properties," *Nature* **402***, 60 (1999).

J.J. Greffet, R. Carminati, K. Joulain, J.P. Mulet, S. Mainguy, and Y. Chen, "Coherent Emission of Light by Thermal Sources," *Nature* **416**, 61–64 (2002).

T.C. Harman, P.J. Taylor, M.P. Walsh, and B.E. LaForge, "Quantum Dot Superlattice Thermoelectric Materials and Devices," *Science* **297**, 2229–2232 (2002).

L.D. Hicks and M.S. Dresselhaus, "The Effect of Quantum Well Structure of the Thermoelectric Figure of Merit," *Phys. Rev. B* **47**, 12727–12731 (1993).

K.F. Hsu, S. Loo, W. Chen, J.S. Dyck, C. Uher, T. Hogan, E.K. Polychroniadis, and M.G. Kanatzidis, "Cubic AgPbSbTe Bulk Thermoelectric Materials with High Figure of Merit," *Science* **303**, 818–821 (2004).

D.J. Singh, "Theoretical and Computational Approaches for Identifying and Optimizing Novel Thermoelectric Materials," *Semicond. & Semimetals* **70**, 125–178 (2001).

R. Venkatasubramanian, E. Silvona, T. Colpitts, and B. O'Quinn, "Thin-film Thermoelectric Devices with High Room-temperature Figures of Merit," *Nature* **413**, 597–602 (2001).

MATERIALS ARCHITECTURES FOR SOLAR ENERGY: ASSEMBLING COMPLEX STRUCTURES

Solar energy conversion devices necessarily involve assembly of nanometer-scale structures into meter-sized articles of manufacture. At present, relatively few methods exist for arranging matter cheaply, robustly, and precisely over such a span of length scales. To enable low-cost fabrication of the large areas of solar energy conversion structures that will be needed if solar energy is to contribute significantly to the primary energy supply, methods must be developed for self-assembly and/or bonding of structures over this span of length scales.

EXECUTIVE SUMMARY

Controlling organization of matter across various length scales is critical for inexpensive fabrication of functionally integrated systems for converting solar photons. Self- and directed-assembly are leading strategies for fabricating such systems. The efficiency of solar cells also depends critically on the morphology and structure of the active materials across many length scales — from the nanoscale to the macroscale. New techniques, tools, and design principles are needed to allow optimized, nanostructured materials and photonic structures to be fabricated over large-area substrates. These techniques may be based on kinetically and/or thermodynamically driven self-assembly of tailored building blocks, or alternatively, they may rely upon construction of the active layers and devices using carefully controlled vapor or solution-based deposition methods. Such new materials and systems are also expected to incorporate many of the design principles that operate in biological photosynthetic systems. The synthetic, photocatalytic materials should allow the spatial arrangements of active components, and the "traffic control" of chemical reactants, intermediates, electrons, and products. The ultimate objective of this area of research is to develop low-cost approaches to fabricating the active materials and components of solar photon conversion systems over large-area substrates.

RESEARCH DIRECTIONS

Develop Scalable Deposition Methods for Organic, Inorganic, and Hybrid Building Blocks

Currently, organic and hybrid photovoltaic (PV) cells are fabricated using wet and vapor deposition methods to afford small-area prototype cells. A vigorous research effort is required to develop new approaches for controlled deposition of a variety of building blocks ranging from small organic molecules and polymers to nanocrystalline inorganic semiconductors. These new methods should include novel vapor deposition methods and wet processing techniques, including spin-, dip- and spray-coating, ink-jet and screen printing, and roll-to-roll processing. An important caveat is that the novel deposition methods should allow control of the morphology of the active materials (see next section) and at the same time they need to be scalable to allow large-area solar cells and modules to be constructed.

Materials and Processing Methods to Control Architecture of the Active Materials

As noted above, the morphology of the active layer in organic and hybrid PV cells plays a key role in determining the overall cell efficiency. The active materials need to be tailored and structured in such a way as to optimize the key steps of light absorption, exciton diffusion to interfaces and charge carrier diffusion to electrodes. While significant advances have been made in the development of novel materials and structures for PV applications, considerable effort is needed to learn how to properly self–assemble them, to organize the various structures, and control the morphology of each interface in order to achieve real breakthroughs and realize disruptive technologies that will bring solar cells technology to the point where it is competitive with other power sources.

New approaches and various techniques must be developed for the controlled deposition of photoactive materials with minimum density of defects so that carrier generation, transport, and collection are optimized. Layered structures are needed to allow confinement of excitons. At the same time, a bicontinuous morphology is needed to decrease the distance needed for excitons to diffuse to interfaces (see Figure 60b), and to allow charges to efficiently diffuse to electrode interfaces. For small molecule-based cells, novel vapor deposition methods are needed that will allow control of the nanostructure of the materials being deposited (see Figure 60a). For polymer and hybrid devices, it is anticipated that a combination of deposition methods and control of molecular architecture can be used to tailor the structure of the active materials.
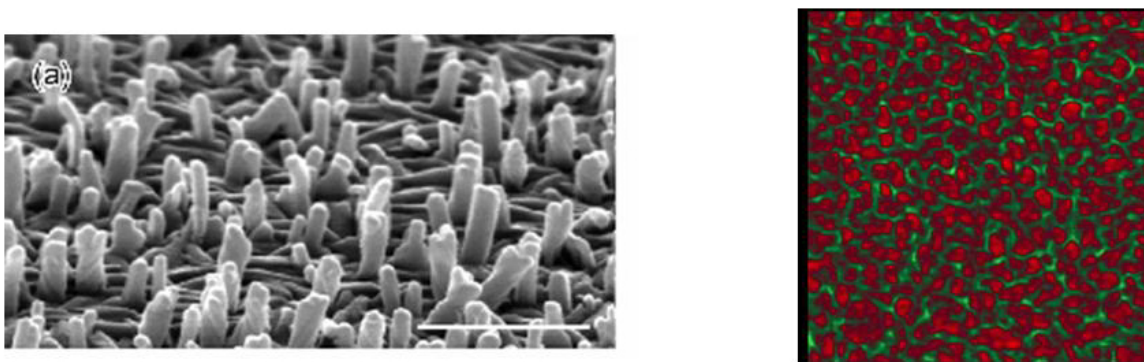

Figure 60 Bulk heterojunction structures. (a) Left: Controlled growth by vapor deposition of a small molecule material into pillars which can give rise bulk heterojunction solar cell material. (b) Right: Bulk heterojunction formed by nanophase segregation of organic PV materials.

Self-assembly

Self-assembly is anticipated to play a substantial role in allowing control of the nano- and mesostructure of the active materials in solar cells constructed from organic, hybrid or inorganic building blocks. For example, by using polymer blends or block polymers, self-assembly can give rise to spontaneous formation of nanostructures that separate donor and acceptor regions allowing for charge carrier diffusion, while maintaining the very high interfacial area needed for effective charge separation. Alternatively, it is anticipated that advances in the ability to control self-assembly of quantum confined structures such as quantum dots and rods may allow for

"bottom-up" construction of inorganic PV materials that are organized on length scales ranging from angstroms (crystal structure) to microns (e.g., superlattice of quantum structures) (see Figure 61). Such assemblies could allow for the simultaneous control of band gap, relative donor-acceptor conduction band energy levels, and the photonic band gap of the material. On even longer length scales, it is anticipated that self-assembly methods could be used to assemble microscale cells into larger solar cell "modules" allowing for easy fabrication of large-area solar arrays that incorporate many miniature multijunction cells.
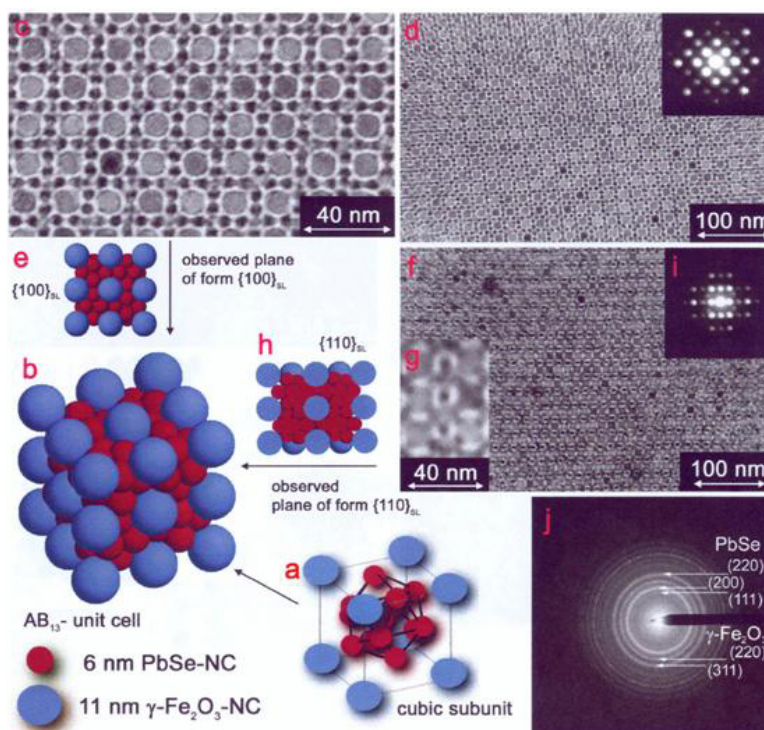

Figure 61 Superlattice formation via self-assembly of inorganic nanocrystals (Source: Redl et al. 2003)

There is also a strong correlation between the structure and morphology of thin-film materials and the nature of the underlying substrate. Issues such as surface crystal morphology, wettability, and surface energy patterning can have a strong influence on the nano- and mesoscale morphology of the deposited film. Fundamental scientific studies need to be carried out to understand how surfaces can be used to gain control over the structure of the PV active layer. Nano- and microscale patterning of a surface can be used to aid self-assembly of cell elements and interconnects.

While some methods have already been developed to allow structural control on the nanoscale of the active materials of organic, hybrid, and inorganic solar cells, considerable new research is needed to develop entirely new approaches. This work will require fundamental scientific studies ranging from a focus on the thermodynamics and kinetics of self-assembly to the development of novel approaches to correlate material structure with macroscale performance in active solar cells. The latter concept will be particularly important in guiding the development of new

materials and fabrication approaches to solar cells. An overall concept that needs to be maintained through all of this work will be scalability. The techniques that are being developed need to able to be both effective and sufficiently rapid to allow low-cost fabrication of large-area, defect-free, PV cell modules.

Approaches to Controlling Light Absorption and Scattering

To achieve high cell conversion efficiency, it is necessary to efficiently capture photons with energies ranging from the visible into the near-infrared (IR). While the intrinsic absorption cross-section of the active materials is important in this regard, advances in cell fabrication are needed to allow the construction of photonic structures that tailor photon energies, and concentrate or confine the optical energy into the active material. A key issue in the construction of active layers for PV cells is that often the active materials need to be thin (*ca.* 100 nm) because of the relatively short exciton diffusion distance. Consequently, strategies are needed that concentrate or capture incident light in order to increase the interaction time or length with the active material (see Figure 62). Structures that combine optical concentration (e.g., integrated lenses or parabolic reflectors) with waveguides could lead to dramatic increases in light-harvesting efficiency. Nonlinear processes such as photon up-conversion or down-conversion could lead to an increase in the quantum efficiency for photon-to-exciton generation. Optical concentrators could substantially increase the probability for nonlinear conversion processes.
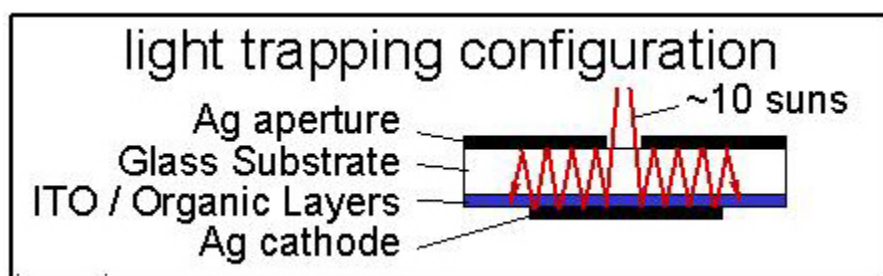

Figure 62 Light-trapping by concentrator/waveguide structure increases light absorption efficiency.

New methods for the deposition of organic, inorganic, and hybrid structures on rigid and flexibles substrates must be developed. These involve both wet and vapor deposition techniques that are easily scalable and that will allow the proper stacking of active structures on both rigid and plastic substrates. Various strategies can be employed using composite and hybrid structures that are tailored, for instance, for self-assembly. Novel approaches to control the PV architecture include, for example, the use of block co-polymers, blends, crystal engineering, as well as using templated nanowires and quantum dots. Methods of controlling light absorption and scattering phenomena through the use of photonic band structures, plasmonic structures and spectral splitting need to be discovered. With this level of control, cell efficiencies have the potential of being enhanced by adopting methods to localize the optical energy directly at or near the exciton dissociation zone.

Self-organized Hierarchical Structures

Biological systems employ a hierarchical organization to carry out many functions, including those of photosynthesis. Chemical processes such as microphase separation in block copolymers, template-directed sol-gel synthesis of porous materials, layer-by-layer synthesis, and nanoparticle self- and directed-assembly (see Figure 63) have opened the door to a vast variety of hierarchical structures that are organized on several length scales. The challenge is to map these new synthesis techniques onto the demands of artificial photosynthesis in order to better control light-harvesting; charge separation; traffic control of holes, electrons, and molecules; catalytic reactions; and permanent separation of the photogenerated fuel and oxidant. A detailed understanding of the kinetics of the processes in complex multicomponent systems (e.g., self-assembled polymer cells, quantum dot sensitized solar cells, organic-inorganic hybrid cells, and solar-fuel conversion systems) is essential to their rational design and utilization in efficient photochemical energy conversion.
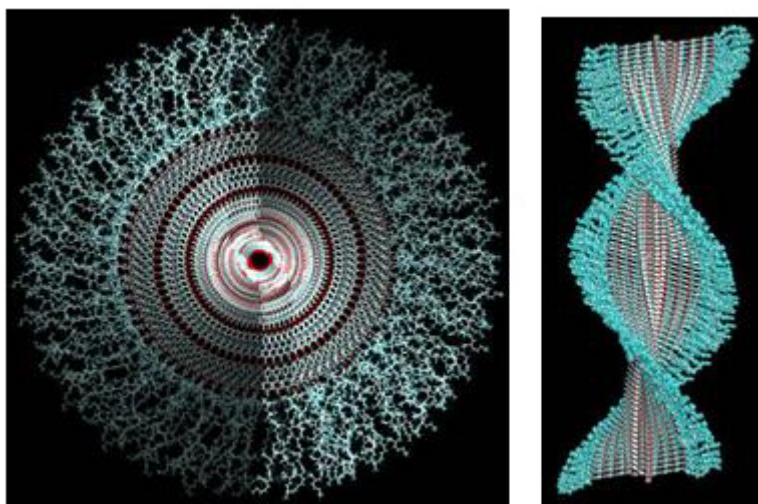

Figure 63 Self-assembling organic nanoribbons (Source: S. Stupp, Northwestern University, unpublished)

For example, visible light-driven water-splitting or CO_2 reduction with high efficiency is currently achieved only in the presence of sacrificial reagents. The design of new photocatalysts that obviate the need for sacrificial reagents is imperative for achieving efficient solar fuel producing assemblies. Structured assemblies need to be developed that allow organization of the active units (e.g., light-harvesting, charge conduction, chemical transport, and selective chemical transformation) for optimum coupling for efficient fuel production. One class of such assemblies are 3-D high-surface-area inert supports that allow precise spatial arrangement of the active components in a predetermined way for optimum coupling and protection from undesired chemistries. These supports (see Figure 64) should have structural elements (walls, membranes) that allow separation of primary redox products on the nanometer scale to prevent undesired cross-reactions and facilitate prompt escape of the products from the fuel forming sites. Catalytic sites should be separated in such a way that energy-rich products, such as hydrogen and oxygen, cannot recombine thermally. A few molecular catalytic components are currently available for

multi-electron H_2O and CO_2 activation, but methods are lacking that allow coupling of these components to electron/hole conducting moieties in 3-D frameworks. Molecular-type linkages need to be developed for efficient charge conduction between catalytic sites and photoactive components embedded in the assembly.

Integrated Time-resolved Probes

Current research on self-assembly has been limited to observation of ordered structures using conventional techniques such as X-ray and electron diffraction, transmission electron microscopy, and atomic force microscopy. Moving self-assembly science forward requires
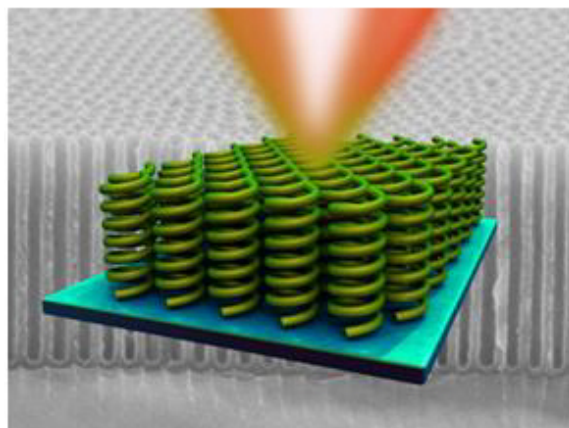

Figure 64 Hierarchical assembly of mesoporous oxide within nanoscopic channels of porous alumina membrane. This example illustrates principles of multiple length ordering.

an experimental window that reveals the three-dimensional structural nature, and time scales of the "embryonic nuclei" that trigger self-assembling processes as they cross from the nanoscale to microscopic and macroscopic dimensions. It is equally critical to observe in real time and space the transformations and intermediate states that assemblies go through before reaching their final form. This information is not presently accessible, and requires invention of "integrated" time-resolved probes that record in real time the evolution of the system across length scales. These might be presently unknown hybrids of scanning probe techniques, near-field strategies, confocal microscopy, magnetic resonance imaging, tomographic techniques, vibrational spectroscopies, and others. Opening this spatial and temporal window on self-assembling systems will allow us to direct systems externally (e.g., through solvent, temperature, external fields, and photons) into the desired targets. A grand challenge is to develop such probes for "self-assembly dynamics" that tolerate compositionally controlled atmospheres, liquid phases, variable temperature, and variable pressure.

New Computational Approaches

New computational approaches are needed to integrate simulations across disparate time and length scales that are important for assembly of solar fuel/energy producing systems (see Figure 65). For example, modeling has traditionally been carried out separately for increments of length scales using quantum mechanics (0.1–10 nm), statistical mechanics (1–1,000 nm), mesoscale (0.1–100 μm), and continuum mechanics (1 mm–10 m). Time scales range from quantum mechanical methods (10^{-15} s) to continuum methods (1–10^5 s). There is a critical need for theoretical modeling and simulation (TMS) to span all these length and time scales seamlessly to meet the needs of solar research, to provide insight into the forces and processes that control the organization of functional elements over all length and time scales; to understand quantitatively the kinetics of catalyzed photochemical energy conversion reactions over many length scales in complex, hybrid systems; to identify active sites on nanostructured surfaces, etc.

TMS will be used to discover the design rules for reverse-engineering building blocks capable of self-assembling into target structures.

SCIENTIFIC CHALLENGES

Presently, there exist many scientific challenges that should be addressed before the ultimate goal can be achieved. Here, inexpensive and simple self-assembly techniques need to be developed for the fabrication of efficient, large-area, low-cost solar cells. The thermodynamic and kinetic principles for integration and self-assembly of different materials should be exploited. The principles of self-assembly to deposit materials (e.g., low-dimensional nanostructures, organic heterostructures, nanocomposites) onto rigid and flexible substrates should be investigated. The science of manipulating interfacial structures and properties, and processing functional materials and structures to optimize optical absorption throughout the solar spectrum, exciton formation and migration towards the proper interface, charge separation, transport, and collection should be established.
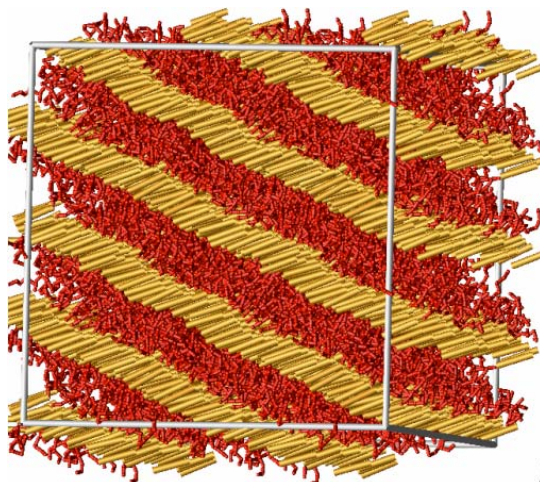

Figure 65 Theoretical simulation for nanorod self-organization into smectic phase (Source: S. Glotzer, University of Michigan, unpublished)

POTENTIAL IMPACT

Ultimately, these efforts would lead to revolutionary multi-functional systems that are capable of light-harvesting, charge separation, molecular transport, fuel production, and chemical separation. This research direction impacts not only the potential efficiency of the solar cell construction, but also the quality. The objective of providing control over morphology and assembly directly impacts a wide range of length scales that can lead to defect-free, high-quality solar photon conversion devices that can be readily produced on a large scale.

REFERENCES

S. Glotzer, University of Michigan, personal communication.

F.X. Redl, K.-S. Cho, C.B. Murray, and S. O'Brien, "Three-dimensional Binary Superlattices of Magnetic Nanocrystals and Semiconductor Quantum Dots," *Nature* **423**, 968 (2003).

S. Stupp, Northwestern University, personal communication.