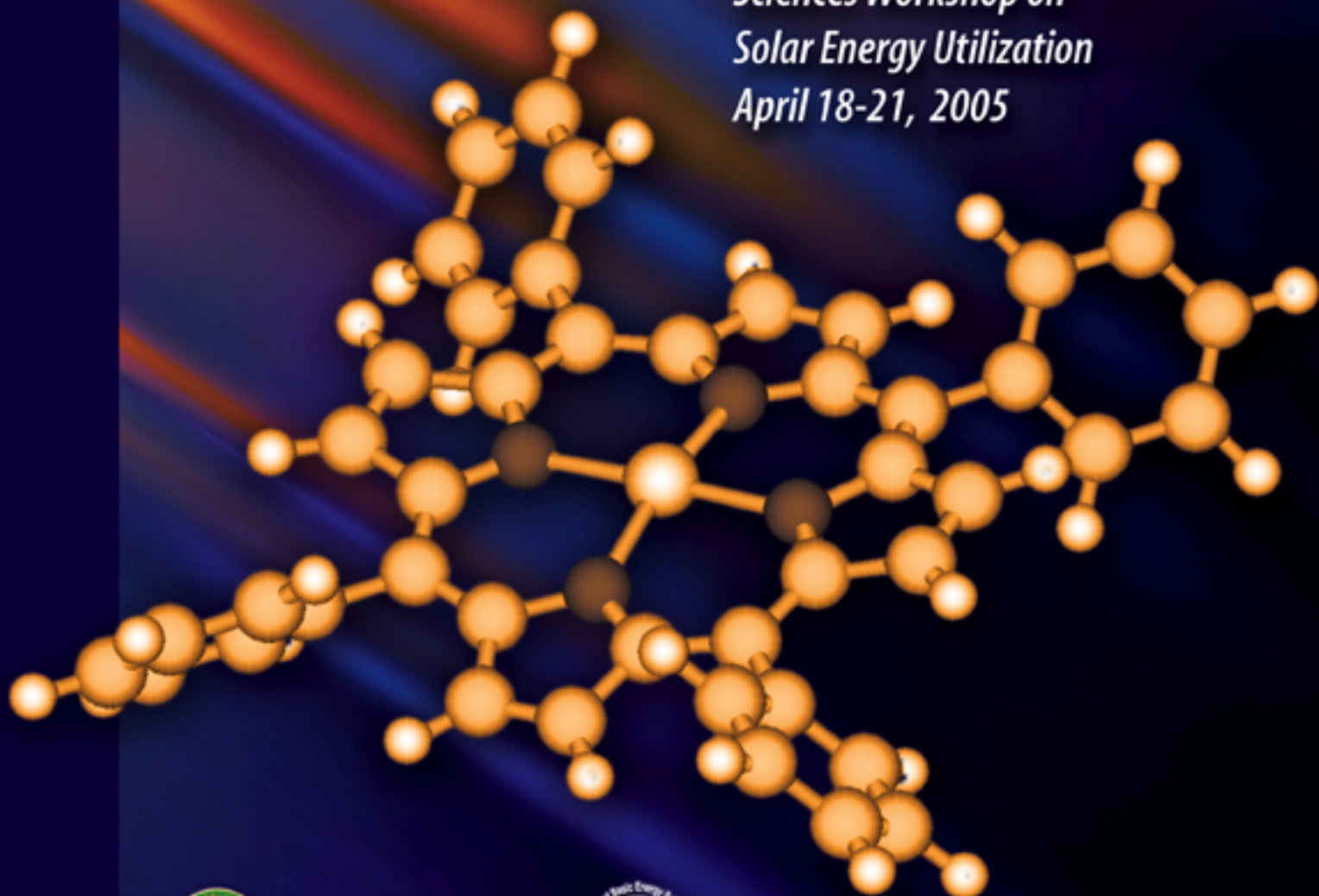# Basic Research Needs for Solar Energy Utilization

Report of the Basic Energy Sciences Workshop on Solar Energy Utilization April 18-21, 2005

Office of Science
U.S. DEPARTMENT OF ENERGY

On the Cover:

One route to harvesting the energy of the sun involves learning to mimic natural photosynthesis. Here, sunlight falls on a porphyrin, one member of a family of molecules that includes the chlorophylls, which play a central role in capturing light and using its energy for photosynthesis in green plants.

Efficient light-harvesting of the solar spectrum by porphyrins and related molecules can be used to power synthetic molecular assemblies and solid-state devices — applying the principles of photosynthesis to the production of hydrogen, methane, ethanol, and methanol from sunlight, water, and atmospheric carbon dioxide.

BASIC RESEARCH NEEDS FOR SOLAR ENERGY UTILIZATION

Report on the Basic Energy Sciences Workshop
on
Solar Energy Utilization

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This report is available on the web at *http://www.sc.doe.gov/bes/reports/files/SEU_rpt.pdf*.

CONTENTS

CONTENTS (CONT.)

NOTATION

ACRONYMS AND ABBREVIATIONS

a-Si:H	hydrogenated amorphous silicon
AD	anaerobic digester
AEZ	agro ecological zone
AM	air mass
ASF	Anderson, Schultz, and Flory
BOS	balance of system
CB	conduction band
CHP	combined heat and power
COP	coefficient of performance
CPV	concentrated photovoltaic
dc	direct current
DNA	deoxyribonucleic acid
DNI	direct normal irradiation
DOE	U.S. Department of Energy
EFG	edge-defined film-fed growth
EIA	Energy Information Administration
EPV	electrochemical photovoltaic
F-T	Fischer-Tropsch
FTL	Fischer-Tropsch liquid
HCPV	high-concentration photovoltaic
HHV	higher heating value
IPCC	Intergovernmental Panel on Climate Change
IR	infrared
LFG	landfill gas
LH1/LH2	light-harvesting pigment/protein complexes
MBE	molecular beam epitaxy
MEG	multiple exciton generation
MESP	minimum ethanol selling price
MOCVD	metalorganic chemical vapor deposition
NAE	National Academy of Engineering
NHE	normal hydrogen electrode
NRC	National Research Council

OEC	oxygen-evolving complex
PCET	proton-coupled electron transfer
PCM	phase change storage material
PEC	photoelectrochemical
PEM	proton exchange membrane
PRD	priority research directions
PSI	photosystem I
PSII	photosystem II
PV	photovoltaic
R&D	research and development
RC	reaction center
TCO	transparent conducting oxide
TMS	theoretical modeling and simulation
TPV	thermophotovoltaic
U.S.	United States
UV	ultraviolet
XAFS	X-ray absorption fine-structure (spectroscopy)
ZT	thermoelectric figure of merit

UNITS OF MEASURE

°C	degree(s) Celsius
$/kW	dollar(s) per kilowatt
μm	micrometer(s)
μs	microsecond(s)
Å	angstrom(s)
amp	ampere(s)
Bbl	billion barrels
cm	centimeter(s)
cm/min	centimeter(s) per minute
eV	electron volt(s)
fs	femtosecond(s)
gal	gallon(s)
Gha	gigahectare(s)
GJ	gigajoule(s)
Gtons	gigatons (10^9 tons = 1 billion tons)
GW	gigawatt(s) (10^9 W = 1 billion watts)
kg	kilogram(s)
kWh	kilowatt hour(s)
kWth	kilowatt(s) (thermal)

K	Kelvin
L	liter(s)
MHz	megahertz
mm	millimeter(s)
MW	megawatt(s) (10^6 W = 1 million watts)
MWe	megawatt(s) (electric)
MWth	megawatt(s) (thermal)
MW/yr	megawatt(s) per year
nm	nanometer(s)
nm/s	nanometer(s) per second
ps	picosecond(s)
psi	pound(s) per square inch
s	second(s)
TW	terawatt(s) (10^{12} W = 1 trillion watts)
W	watt(s)
W_p	peak watt(s)
yr	year(s)

EXECUTIVE SUMMARY

World demand for energy is projected to more than double by 2050 and to more than triple by the end of the century. Incremental improvements in existing energy networks will not be adequate to supply this demand in a sustainable way. Finding sufficient supplies of clean energy for the future is one of society's most daunting challenges.

Sunlight provides by far the largest of all carbon-neutral energy sources. More energy from sunlight strikes the Earth in one hour (4.3×10^{20} J) than all the energy consumed on the planet in a year (4.1×10^{20} J). We currently exploit this solar resource through solar electricity — a $7.5 billion industry growing at a rate of 35–40% per annum — and solar-derived fuel from biomass, which provides the primary energy source for over a billion people.

Yet solar electricity currently provides only approximately 1 millionth of the total electricity supply, and renewable biomass provides less than 0.1% of total energy consumed. The huge gap between our present use of solar energy and its enormous undeveloped potential defines a grand challenge in energy research. Sunlight is a compelling solution to our need for clean, abundant sources of energy in the future. It is readily available, secure from geopolitical tension, and poses no threat to our environment through pollution or to our climate through greenhouse gases.

This report of the Basic Energy Sciences Workshop on Solar Energy Utilization identifies the key scientific challenges and research directions that will enable efficient and economic use of the solar resource to provide a significant fraction of global primary energy by the mid 21st century. The report reflects the collective output of the workshop attendees, which included 200 scientists representing academia, national laboratories, and industry in the United States and abroad, and the U.S. Department of Energy's Office of Basic Energy Sciences and Office of Energy Efficiency and Renewable Energy.

Solar energy conversion systems fall into three categories according to their primary energy product: solar electricity, solar fuels, and solar thermal systems. Each of the three generic approaches to exploiting the solar resource has untapped capability well beyond its present usage. Workshop participants considered the potential of all three approaches, as well as the potential of hybrid systems that integrate key components of individual technologies into novel cross-disciplinary paradigms.

SOLAR ELECTRICITY

The challenge in converting sunlight to electricity via photovoltaic solar cells is dramatically reducing the cost/watt of delivered solar electricity — by approximately a factor of 5–10 to compete with fossil and nuclear electricity and by a factor of 25–50 to compete with primary fossil energy. New materials to efficiently absorb sunlight, new techniques to harness the full spectrum of wavelengths in solar radiation, and new approaches based on nanostructured architectures can revolutionize the technology used to produce solar electricity. The technological development and successful commercialization of single-crystal solar cells demonstrates the promise and practicality of photovoltaics, while novel approaches exploiting

thin films, organic semiconductors, dye sensitization, and quantum dots offer fascinating new opportunities for cheaper, more efficient, longer-lasting systems. Many of the new approaches outlined by the workshop participants are enabled by (1) remarkable recent advances in the fabrication of nanoscale architectures by novel top-down and bottom-up techniques; (2) advances in nanoscale characterization using electron, neutron, and x-ray scattering and spectroscopy; and (3) sophisticated computer simulations of electronic and molecular behavior in nanoscale semiconductor assemblies using density functional theory. Such advances in the basic science of solar electric conversion, coupled to the new semiconductor materials now available, could drive a revolution in the way that solar cells are conceived, designed, implemented, and manufactured.

SOLAR FUELS

The inherent day-night and sunny-cloudy cycles of solar radiation necessitate an effective method to store the converted solar energy for later dispatch and distribution. The most attractive and economical method of storage is conversion to chemical fuels. The challenge in solar fuel technology is to produce chemical fuels directly from sunlight in a robust, cost-efficient fashion.

For millennia, cheap solar fuel production from biomass has been the primary energy source on the planet. For the last two centuries, however, energy demand has outpaced biomass supply. The use of existing types of plants requires large land areas to meet a significant portion of primary energy demand. Almost all of the arable land on Earth would need to be covered with the fastest-growing known energy crops, such as switchgrass, to produce the amount of energy currently consumed from fossil fuels annually. Hence, the key research goals are (1) application of the revolutionary advances in biology and biotechnology to the design of plants and organisms that are more efficient energy conversion "machines," and (2) design of highly efficient, all-artificial, molecular-level energy conversion machines exploiting the principles of natural photosynthesis. A key element in both approaches is the continued elucidation — by means of structural biology, genome sequencing, and proteomics — of the structure and dynamics involved in the biological conversion of solar radiation to sugars and carbohydrates. The revelation of these long-held secrets of natural solar conversion by means of cutting-edge experiment and theory will enable a host of exciting new approaches to direct solar fuel production. Artificial nanoscale assemblies of new organic and inorganic materials and morphologies, replacing natural plants or algae, can now use sunlight to directly produce H_2 by splitting water and hydrocarbons via reduction of atmospheric CO_2. While these laboratory successes demonstrate the appealing promise of direct solar fuel production by artificial molecular machines, there is an enormous gap between the present state of the art and a deployable technology. The current laboratory systems are unstable over long time periods, too expensive, and too inefficient for practical implementation. Basic research is needed to develop approaches and systems to bridge the gap between the scientific frontier and practical technology.

SOLAR THERMAL SYSTEMS

The key challenge in solar thermal technology is to identify cost-effective methods to convert sunlight into storable, dispatchable thermal energy. Reactors heated by focused, concentrated sunlight in thermal towers reach temperatures exceeding 3,000°C, enabling the efficient chemical production of fuels from raw materials without expensive catalysts. New materials that withstand the high temperatures of solar thermal reactors are needed to drive applications of this technology. New chemical conversion sequences, like those that split water to produce H_2 using the heat from nuclear fission reactors, could be used to convert focused solar thermal energy into chemical fuel with unprecedented efficiency and cost effectiveness. At lower solar concentration temperatures, solar heat can be used to drive turbines that produce electricity mechanically with greater efficiency than the current generation of solar photovoltaics. When combined with solar-driven chemical storage/release cycles, such as those based on the dissociation and synthesis of ammonia, solar engines can produce electricity continuously 24 h/day. Novel thermal storage materials with an embedded phase transition offer the potential of high thermal storage capacity and long release times, bridging the diurnal cycle. Nanostructured thermoelectric materials, in the form of nanowires or quantum dot arrays, offer a promise of direct electricity production from temperature differentials with efficiencies of 20–30% over a temperature differential of a few hundred degrees Celsius. The much larger differentials in solar thermal reactors make even higher efficiencies possible. New low-cost, high-performance reflective materials for the focusing systems are needed to optimize the cost effectiveness of all concentrated solar thermal technologies.

PRIORITY RESEARCH DIRECTIONS

Workshop attendees identified thirteen priority research directions (PRDs) with high potential for producing scientific breakthroughs that could dramatically advance solar energy conversion to electricity, fuels, and thermal end uses. Many of these PRDs address issues of concern to more than one approach or technology. These cross-cutting issues include (1) coaxing cheap materials to perform as well as expensive materials in terms of their electrical, optical, chemical, and physical properties; (2) developing new paradigms for solar cell design that surpass traditional efficiency limits; (3) finding catalysts that enable inexpensive, efficient conversion of solar energy into chemical fuels; (4) identifying novel methods for self-assembly of molecular components into functionally integrated systems; and (5) developing materials for solar energy conversion infrastructure, such as transparent conductors and robust, inexpensive thermal management materials.

A key outcome of the workshop is the sense of optimism in the cross-disciplinary community of solar energy scientists spanning academia, government, and industry. Although large barriers prevent present technology from producing a significant fraction of our primary energy from sunlight by the mid-21st century, workshop participants identified promising routes for basic research that can bring this goal within reach. Much of this optimism is based on the continuing, rapid worldwide progress in nanoscience. Powerful new methods of nanoscale fabrication, characterization, and simulation — using tools that were not available as little as five years ago — create new opportunities for understanding and manipulating the molecular and electronic pathways of solar energy conversion. Additional optimism arises from impressive strides in

genetic sequencing, protein production, and structural biology that will soon bring the secrets of photosynthesis and natural bio-catalysis into sharp focus. Understanding these highly effective natural processes in detail will allow us to modify and extend them to molecular reactions that directly produce sunlight-derived fuels that fit seamlessly into our existing energy networks. The rapid advances on the scientific frontiers of nanoscience and molecular biology provide a strong foundation for future breakthroughs in solar energy conversion.

INTRODUCTION

INTRODUCTION

The supply and demand of energy determine the course of global development in every sphere of human activity. Sufficient supplies of clean energy are intimately linked with global stability, economic prosperity, and quality of life. Finding energy sources to satisfy the world's growing demand is one of society's foremost challenges for the next half-century. The importance of this pervasive problem and the perplexing technical difficulty of solving it require a concerted national effort marshalling our most advanced scientific and technological capabilities.

THE ENERGY CHALLENGE

The world now uses energy at a rate of approximately 4.1×10^{20} joules/yr, equivalent to a continuous power consumption of 13 trillion watts, or 13 terawatts (TW). Even with aggressive conservation and energy efficiency measures, an increase of the Earth's population to 9 billion people, accompanied by rapid technology development and economic growth world-wide, is projected to produce more than double the demand for energy (to 30 TW) by 2050, and more than triple the demand (to 46 TW) by the end of the century. The reserves of fossil fuels that currently power society will fall short of this demand over the long term, and their continued use produces harmful side effects such as pollution that threatens human health and greenhouse gases associated with climate change. Alternative renewable fuels are at present far from competitive with fossil fuels in cost and production capacity. Without viable options for supplying double or triple today's energy use, the world's economic, technological, and political horizons will be severely limited.

SOLAR ENERGY

Our primary source of clean, abundant energy is the sun. The sun deposits 120,000 TW of radiation on the surface of the Earth, far exceeding human needs even in the most aggressive energy demand scenarios. The sun is Earth's natural power source, driving the circulation of global wind and ocean currents, the cycle of water evaporation and condensation that creates rivers and lakes, and the biological cycles of photosynthesis and life. Covering 0.16% of the land on Earth with 10% efficient solar conversion systems would provide 20 TW of power, nearly twice the world's consumption rate of fossil energy and the equivalent 20,000 1-GW_e nuclear fission plants. These comparisons illustrate the impressive magnitude of the solar resource, providing an energy stream far more potent than present-day human technology can achieve.

All routes for utilizing solar energy exploit the functional steps of *capture, conversion,* and *storage*. The sun's energy arrives on Earth as radiation distributed across the color spectrum from infrared to ultraviolet. The energy of this radiation must be captured as excited electron-hole pairs in a semiconductor, a dye, or a chromophore, or as heat in a thermal storage medium. Excited electrons and holes can be tapped off for immediate conversion to electrical power, or transferred to biological or chemical molecules for conversion to fuel. Natural photosynthesis produces fuel in the form of sugars and other carbohydrates derived from the reduction of CO_2 in the atmosphere and used to power the growth of plants. The plants themselves become available

as biomass for combustion as primary fuels or for conversion in reactors to secondary fuels like liquid ethanol or gaseous carbon monoxide, methane, and hydrogen. We are now learning to mimic the natural photosynthetic process in the laboratory using artificial molecular assemblies, where the excited electrons and holes can drive chemical reactions to produce fuels that link to our existing energy networks. Atmospheric CO_2 can be reduced to ethanol or methane, or water can be split to create hydrogen. These fuels are the storage media for solar energy, bridging the natural day-night, winter-summer, and cloudy-sunny cycles of solar radiation.

In addition to electric and chemical conversion routes, solar radiation can be converted to heat energy. Solar concentrators focus sunlight collected over a large area to a line or spot where heat is collected in an absorber. Temperatures as high as 3,000°C can be generated to drive chemical reactions, or heat can be collected at lower temperatures and transferred to a thermal storage medium like water for distributed space heating or steam to drive an engine. Effective storage of solar energy as heat requires developing thermal storage media that accumulate heat efficiently during sunny periods and release heat slowly during dark or cloudy periods. Heat is one of the most versatile forms of energy, the common link in nearly all our energy networks. Solar thermal conversion can replace much of the heat now supplied by fossil fuel.

Although many routes use solar energy to produce electricity, fuel, and heat, none are currently competitive with fossil fuels for a combination of cost, reliability, and performance. Solar electricity from photovoltaics is too costly, by factors of 5–10, to compete with fossil-derived electricity, and is too costly by factors of 25–50 to compete with fossil fuel as a primary energy source. Solar fuels in the form of biomass produce electricity and heat at costs that are within range of fossil fuels, but their production capacity is limited. The low efficiency with which they convert sunlight to stored energy means large land areas are required. To produce the full 13 TW of power used by the planet, nearly all the arable land on Earth would need to be planted with switchgrass, the fastest-growing energy crop. Artificial photosynthetic systems are promising routes for converting solar energy to fuels, but they are still in the laboratory stage where the principles of their assembly and functionality are being explored. Solar thermal systems provide the lowest-cost solar electricity at the present time, but require large areas in the Sun Belt and breakthroughs in materials to become economically competitive with fossil energy as a primary energy source. While solar energy has enormous promise as a clean, abundant, economical energy source, it presents formidable basic research challenges in designing materials and in understanding the electronic and molecular basis of capture, conversion, and storage before its promise can be realized.

THE WORKSHOP ON SOLAR ENERGY UTILIZATION

The U.S. Department of Energy (DOE) Office of Basic Energy Sciences held a Workshop on Solar Energy Utilization on April 18–21, 2005, in Bethesda, Maryland, to examine the challenges and opportunities for the development of solar energy as a competitive energy source. The workshop brought together 200 participants representing the basic science and technology of solar energy utilization. Participants were drawn from academia, industry, and national laboratories in the United States, Europe, and Asia, with interdisciplinary expertise spanning physics, chemistry, biology, materials, and engineering. Their charge was to identify the technical barriers to large-scale implementation of solar energy and the basic research directions

showing promise to overcome them. The workshop focused on the grand challenges in solar energy research, where scientific breakthroughs will produce revolutionary, not evolutionary, progress in bringing solar conversion a significant share of the energy marketplace.

The workshop comprised panels that examined the conversion of solar energy into three end products: solar electricity, solar fuels, and solar thermal conversion. The chairs of the panels and subpanels were drawn from universities, research institutions, and national laboratories. Pat Dehmer, Director of DOE's Office of Basic Energy Sciences, launched the opening plenary session of the workshop, presenting the charge to participants and the scope. Energy experts from academia and industry set the stage with plenary talks on future energy demand, potential sources of supply, the impact of energy on environment, and the status of commercial solar technologies. Scientists from the DOE's Office of Energy Efficiency and Renewable Energy briefed the participants on the accomplishments and outlook for its solar energy programs. The chairs of the workshop panels presented the current scientific status and the grand challenges in solar electric, solar fuels, and solar thermal conversion.

Following the opening plenary session, the participants divided into panels and subpanels examining solar electric, solar fuels, and solar thermal conversion options (see Appendix 3 for the workshop schedule). Each of these panels invited expert speakers to analyze the grand challenges and scientific routes to achieve them. The sub-panels then developed a set of high-priority research directions with potential to produce revolutionary, not evolutionary, breakthroughs in materials and processes for solar energy utilization. These Priority Research Directions (PRDs) are the major output of the workshop and are presented in this report.

SOLAR ENERGY OUTLOOK

The scientific stage is set for rapid progress in solar energy research. The last five years have seen rapid advances in nanoscience and nanotechnology, allowing unprecedented manipulation of the nanoscale structures controlling solar capture, conversion, and storage. Light interacts with materials on the scale of its wavelength, a few hundred nanometers. Energy capture occurs via excited electron states confined by defect structures or interfaces to dimensions of tens of nanometers. Conversion of excited electrons to fuels such as ethanol, methane, or hydrogen occurs in chemical reactions at the scale of molecules. These nanoscale processes have never been more accessible to observation and manipulation. Advances in fabrication of nanoscale structures by top-down lithography and bottom-up self-assembly are rapidly broadening our horizons for creating and interconnecting the functional units for capture, conversion, and storage of solar energy. Parallel advances in experimental tools that probe complex systems at ever shorter length and time scales by electron, X-ray, and neutron scattering at major facilities and by the explosion of scanning probe microscopies at the benchtop are now revealing secrets of electron transfer, catalytic activity, and chemical transformation that have long been hidden. Advances in density functional theory coupled with multinode computational clusters now enable accurate simulation of the behavior of multithousand atom complexes that mediate the electronic and ionic transfers of solar energy conversion. These new and emerging nanoscience capabilities bring a fundamental understanding of the atomic and molecular processes of solar energy utilization within reach.

The revolution in biology is a second major force enabling rapid progress in solar energy research. The twin triumphs of genome sequencing and protein production promise unprecedented control of the natural assembly process of photosynthetic systems, with deeper insights into the role of specific proteins in mediating specific functions. Natural photosystems show remarkable robustness, often functioning effectively for decades through sophisticated systems of protein repair and replacement, and by implementing defect-tolerant networks of redundancy. We are on the verge of understanding these powerful natural longevity mechanisms, and of applying them to our own designs for synthetic molecular machines. Self-repair and defect tolerance are powerful new paradigms that we can adapt from nature to extend the life of artificial solar conversion systems by many decades. Structural biology now allows determination of the atomic positions of biocatalysts like hydrogenase and the solar water-splitting complex in Photosystem II to the 3.5 Å level. Such information brings us tantalizingly close to the ability to reproduce their structures and functions artificially. This is the kind of breakthrough that will generate qualitatively new routes to solar energy conversion: deconstruction of natural solar energy converters followed by reconstruction of artificial variants that maximize targeted objectives. While such scientific capability is within sight, bringing it within reach requires further breakthroughs in biology and nanoscience.

THE REPORT

This report presents information on several levels. The Executive Summary describes the motivation and challenge of meeting world energy demands over the next century with the solar resource. It presents in capsule form the research opportunities and the scientific gaps to making sunlight a significant player in the energy marketplace. The Technology Assessments describe the present state of commercial technology for utilizing solar energy. The Panel Surveys of Solar Electric, Solar Fuel, and Solar Thermal Conversion present the scientific basis of each of these fields and the grand challenges that must be met for solar energy to become competitive with fossil fuel in supplying our energy needs. The Priority Research Directions represent the collective wisdom of the workshop and are its most specific output. They identify the high-priority research directions that address the grand challenges of solar energy utilization and promise revolutionary progress in bringing solar energy to its full potential in the energy marketplace.

GLOBAL ENERGY RESOURCES

GLOBAL ENERGY RESOURCES

Current global energy consumption is 4.1×10^{20} J annually, which is equivalent to an instantaneous yearly-averaged consumption rate of 13×10^{12} W [13 trillion watts, or 13 terawatts (TW)]. Projected population and economic growth will more than double this global energy consumption rate by the mid-21st century and more than triple the rate by 2100, even with aggressive conservation efforts. Hence, to contribute significantly to global primary energy supply, a prospective resource has to be capable of providing at least 1-10 TW of power for an extended period of time.

The threat of climate change imposes a second requirement on prospective energy resources: they must produce energy without the emission of additional greenhouse gases. Stabilization of atmospheric CO_2 levels at even twice their preanthropogenic value will require daunting amounts of carbon-neutral energy by mid-century. The needed levels are in excess of 10 TW, increasing after 2050 to support economic growth for an expanding population.

The three prominent options to meet this demand for carbon-neutral energy are fossil fuel use in conjunction with carbon sequestration, nuclear power, and solar power. The challenge for carbon sequestration is finding secure storage for the 25 billion metric tons of CO_2 produced annually on Earth. At atmospheric pressure, this yearly global emission of CO_2 would occupy 12,500 km^3, equal to the volume of Lake Superior; it is 600 times the amount of CO_2 injected every year into oil wells to spur production, 100 times the amount of natural gas the industry draws in and out of geologic storage in the United States each year to smooth seasonal demand, and 20,000 times the amount of CO_2 stored annually in Norway's Sleipner reservoir. Beyond finding storage volume, carbon sequestration also must prevent leakage. A 1% leak rate would nullify the sequestration effort in a century, far too short a time to have lasting impact on climate change. Although many scientists are optimistic, the success of carbon sequestration on the required scale for sufficiently long times has not yet been demonstrated.

Nuclear power is a second conceptually viable option. Producing 10 TW of nuclear power would require construction of a new one-gigawatt-electric (1-GW$_e$) nuclear fission plant somewhere in the world every other day for the next 50 years. Once that level of deployment was reached, the terrestrial uranium resource base would be exhausted in 10 years. The required fuel would then have to be mined from seawater (requiring the equivalent of 10 Niagara Falls), or else breeder reactor technology would have to be developed and disseminated to countries wishing to meet their additional energy demand in this way.

The third option is to exploit renewable energy sources, of which solar energy is by far the most prominent. United Nations (U.N.) estimates indicate that the remaining global, practically exploitable hydroelectric resource is less than 0.5 TW. The cumulative energy in all the tides and ocean currents in the world amounts to less than 2 TW. The total geothermal energy at the surface of the Earth, integrated over all the land area of the continents, is 12 TW, of which only a small fraction could be practically extracted. The total amount of globally extractable wind power has been estimated by the IPCC and others to be 2-4 TW$_e$. For comparison, the solar constant at the top of the atmosphere is 170,000 TW, of which, on average, 120,000 TW strikes the Earth (the remainder being scattered by the atmosphere and clouds). It is clear that solar

energy can be exploited on the needed scale to meet global energy demand in a carbon-neutral fashion without significantly affecting the solar resource.

Solar energy is diffuse and intermittent, so effective storage and distribution are critical to matching supply with demand. The solar resource has been well established, and the mean yearly insolation values are well documented. At a typical latitude for the United States, a net 10% efficient solar energy "farm" covering 1.6% of the U.S. land area would meet the country's entire domestic energy needs; indeed, just 0.16% of the land on Earth would supply 20 TW of power globally. For calibration purposes, the required U.S. land area is about 10 times the area of all single-family residential rooftops and is comparable with the land area covered by the nation's federally numbered highways. The amount of energy produced by these boxes is equal to that produced by 20,000 1-GWe nuclear fission plants. This many plants would need to be constructed to meet global demands for carbon-neutral energy by the mid-21st century if carbon sequestration were to prove technically nonviable and if solar energy were not developed.

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

BASIC RESEARCH CHALLENGES FOR SOLAR ELECTRICITY

CURRENT STATUS

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

From the mid 1950s to the early 1970s, PV research and development (R&D) was directed primarily toward space applications and satellite power. Then, in 1973, a greatly increased level of R&D on solar cells was initiated following the oil embargo in that year, which caused widespread concern regarding energy supply. In 1976, the U.S. Department of Energy (DOE), along with its Photovoltaics Program, was created. DOE, as well as many other international organizations, began funding PV R&D at appreciable levels, and a terrestrial solar cell industry quickly evolved. Figure 1 shows a plot of annual PV power production vs. time for the period 1988–2003 (Surek 2005). Total global PV (or solar) cell production increased from less than 10 MW_p/yr in 1980 to about 1,200 MW_p/yr in 2004; the current total global PV installed capacity is about 3 GW_p. The "peak watt" (W_p) rating is the power (in watts) produced by a solar module illuminated under the following standard conditions: 1,000 W/m^2 intensity, 25°C ambient temperature, and a spectrum that relates to sunlight that has passed through the atmosphere when the sun is at a 42° elevation from the horizon (defined as air mass [or AM] 1.5;
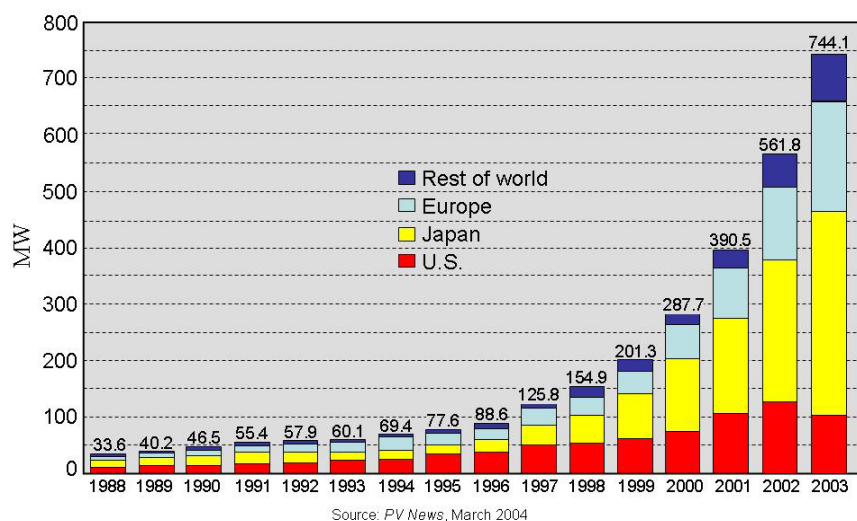

Figure 1 World PV cell/module production (in MW_p)

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

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

In addition to module costs, a PV system also has costs associated with the non-photoactive parts of the system. These are called balance of system (BOS) costs, and they are currently in the range of $250/m^2$ for Generation I cells. Thus, the total cost of present PV systems is about $6/W_p$. Taking into account the cost of capital funds, interest rates, depreciation, system lifetime, and the available annual solar irradiance integrated over the year (i.e., considering the diurnal
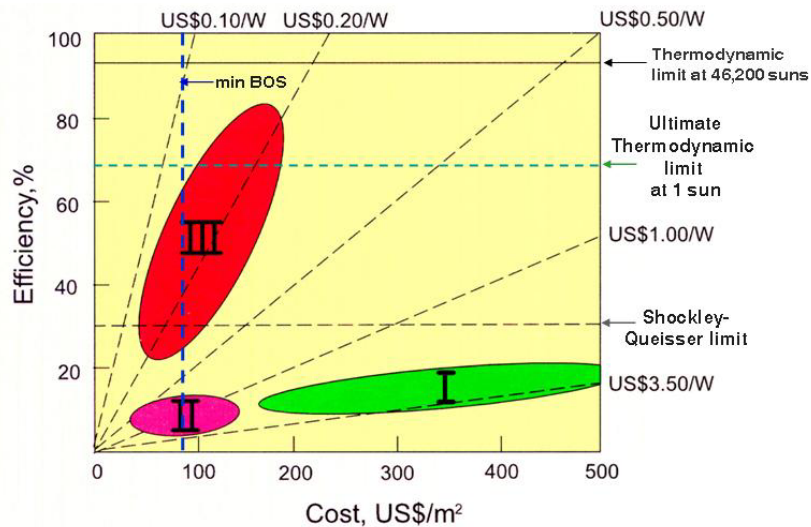
For PV or PEC to provide the full level of C-free energy required for electricity and fuel—solar power cost needs to be ~2 cents/kWh ($0.40/W_p).

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

CONVERSION OF SUNLIGHT INTO ELECTRICITY

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

According to quantum theory, light can behave either as waves or as particles, depending upon the specific interaction of light with matter; this phenomenon is called the wave-particle duality of light. In the particle description, light consists of discrete particle-like packets of energy called photons. Sunlight contains photons with energies that reflect the sun's surface temperature; in energy units of electron volts (eV), the solar photons range in energy (hv) from about 3.5 eV (ultraviolet region) to 0.5 eV (infrared region). The energy of the visible region ranges from 3.0 eV (violet) to 1.8 eV (red); the peak power of the sun occurs in the yellow region of the visible region, at about 2.5 eV. At high noon on a cloudless day, the surface of the Earth receives 1,000 watts of solar power per square meter (1 kW/m^2).
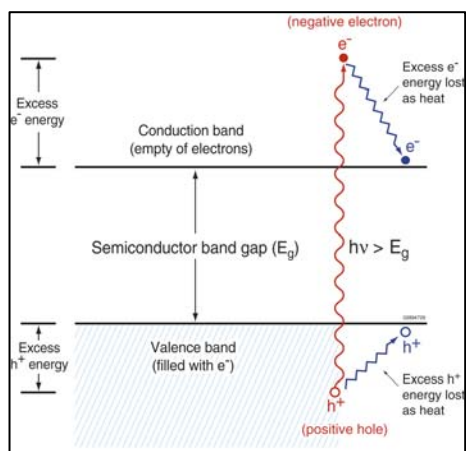
Photovoltaic cells generally consist of a light absorber that will only absorb solar photons above a certain minimum photon energy. This minimum threshold energy is called the "energy gap" or "band gap" (E_g); photons with energies below the band gap pass through the absorber, while photons with energies above the band gap are absorbed. The light absorber in PV cells can be either inorganic semiconductors, organic molecular structures, or a combination of both.

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

When photons are absorbed, they transfer their energy to electrons in the filled valence band and promote these electrons to higher energy states in the empty conduction band. There are no energy states between the valence and conduction bands, which is why this separation is called a band gap and why only photons with energies above the band gap can cause the transfer of electrons from the lower-energy-state valence band into the higher-energy-state

conduction band. When photons transfer electrons across the band gap, they create negative charges in the conduction band and leave behind positive charges in the valence band; these positive charges are called holes (h$^+$). Thus, absorbed photons in semiconductors create pairs of negative electrons and positive holes. In a PV cell, the electrons and holes formed upon absorption of light separate and move to opposite sides of the cell structure, where they are collected and pass through wires connected to the cell to produce a current and a voltage — thus generating electrical power.

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

Furthermore, certain organic polymers and other molecular structures can form organic semiconductors that provide the basis for organic PV devices. One difference between inorganic and organic PV cells is that in organic cells, the electrons and holes are initially bound to each other in pairs called excitons; these excitons must be broken apart in order to separate the electrons and holes to generate electricity. In inorganic PV cells, the electrons and holes created by the absorption of light are not bound together and are free to move independently in the semiconductor.
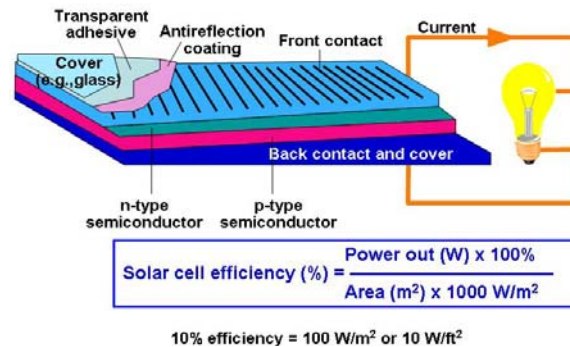
cycle and cloud cover, which produces an average power over a year that is about 1/5 of the peak power rating), the $/W_p$ cost figure of merit can be converted to $/kWh by the following simple relationship: $1/W_p \sim \$0.05$/kWh. This calculation leads to a present cost for grid-connected PV electricity of about $0.30/kWh. Areas labeled II and III in Figure 2 present the module costs for Generation II (thin-film PV) and Generation III (advanced future structures) PV cells.

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

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

PHYSICS OF PHOTOVOLTAIC CELLS

Inorganic PV and electrochemical PV (EPV) cells operate upon the establishment of an electric potential difference between the n- and p-type regions in an inorganic PV cell or between an n- or p-type semiconductor and redox electrolyte, in the case of an EPV cell. This difference creates an electrical diode structure. The current-voltage behavior of such junctions follows the diode equations, in which the current flow in one direction across the junction is constant with voltage, whereas the current flow in the other direction across the junction increases exponentially with the applied voltage. Hence, the dark current density (J_{dark} [amps/cm^2]), as a function of the voltage (V) applied to this diode (assuming ideal diode behavior), is:

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

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

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

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

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

The net current density (J) is:

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

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

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

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

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

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

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

$$FF = J_mV_m/J_{sc}V_{oc} \tag{5}$$

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

The cell conversion efficiency is the electrical power density (J_mV_m) (watts/cm^2) divided by the incident solar power density (P_{sun}), multiplied by 100 to obtain a percent value.
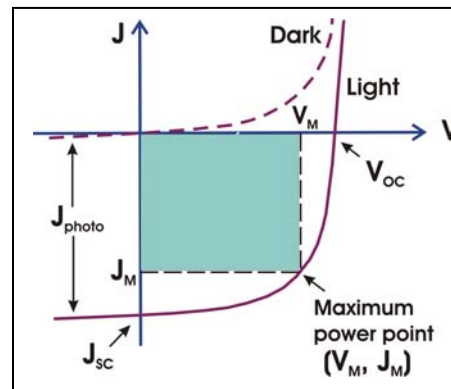
$$\eta = J_mV_m/P_{sun} = 100 * J_{sc}V_{oc} FF/P_{sun} \tag{6}$$
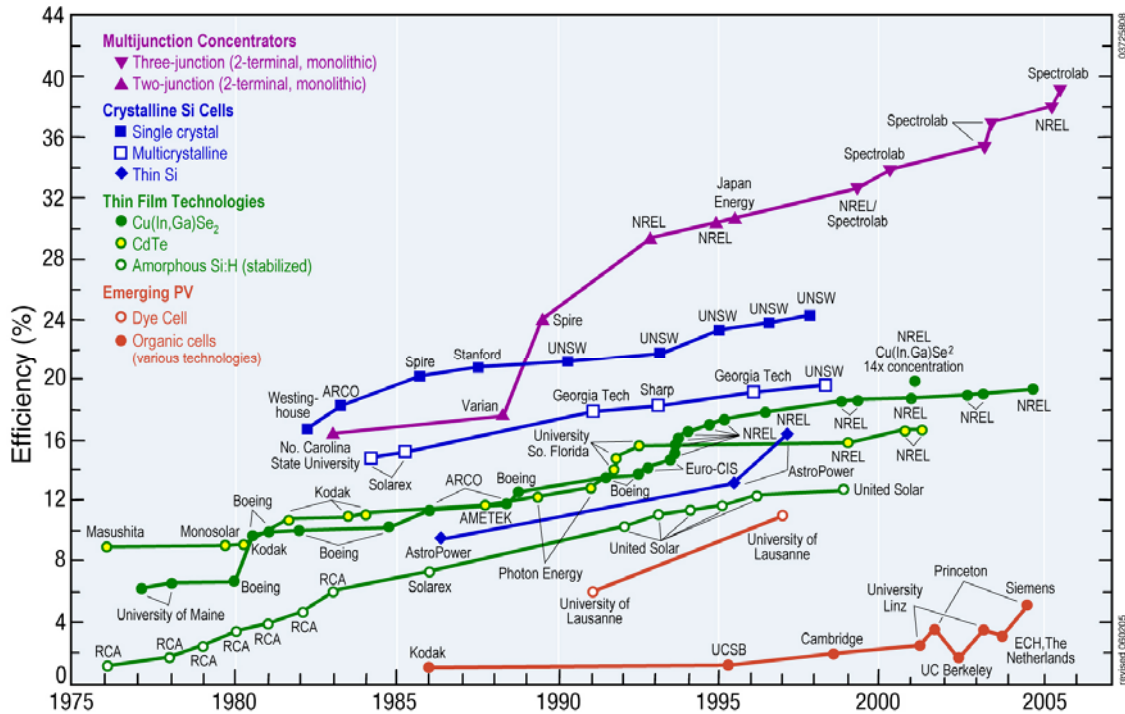
Figure 3 Improvements in solar cell efficiency, by system, from 1976 to 2004

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

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

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

IMPACT OF INEXPENSIVE SOLAR ELECTRICITY

In 2004, the United States consumed approximately 4.0×10^{12} kWh (energy consumed in one year at an average power of 0.46 TW) of electricity (Energy Information Administration [EIA] 2005); this amount represents about 14% of total U.S. energy consumption (EIA 2005). The U.S. electricity produced by solar PV cells currently represents a tiny fraction (<0.02%) of the total electricity supply. The challenge for generators of solar electricity is to produce it at very low cost, ultimately approaching $0.40/W$_p$, which is equivalent to an energy cost of $0.02/kWh. Achieving this cost would require a reduction in the $/W$_p$ price of about a factor of 15–25
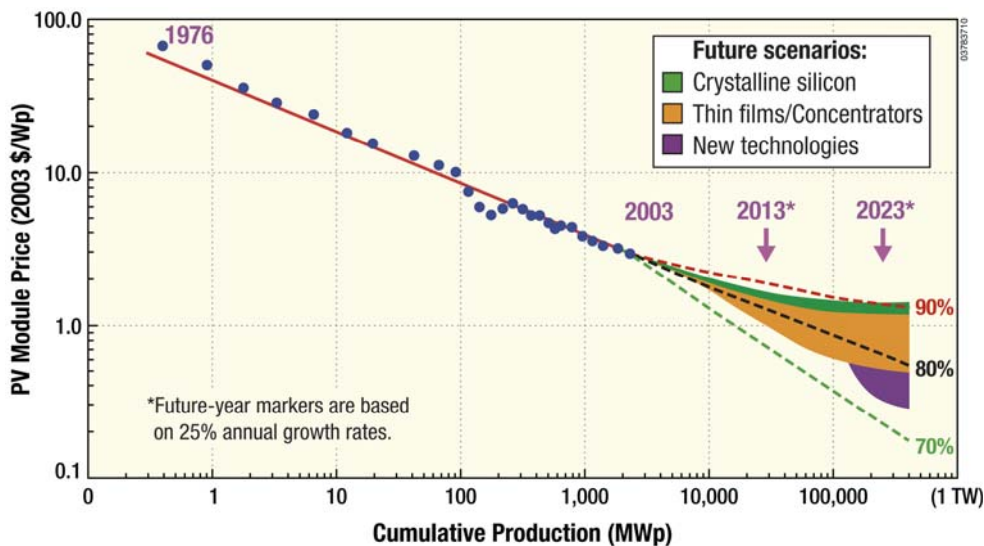
Figure 4 Learning curve for PV production. The present learning curve rate is 80% (20% cost reduction for every doubling of cumulative production); projected rates of 90% and 70% are shown for years beyond 2003. (Source: Surek 2005)

relative to present PV costs. Such a low cost for solar electricity would be expected to result in massive implementation of solar energy systems in the energy infrastructure in the United States and globally. Such a cost breakthrough would also represent a major advance in using solar energy to alleviate the anticipated future problems associated with energy supply, energy security, and unacceptable levels of atmospheric CO_2. In addition to satisfying electrical power needs, solar electricity at \$0.02/kWh could also contribute to the goal of producing cost-effective non-carbonaceous solar fuels, such as hydrogen (National Academy of Engineering, Board on Energy and Environmental Systems 2004). However, to achieve the latter goal, major advances in suitable and scalable storage and distribution technologies will also be required.

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

Need for Revolution on Existing Technology Path

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

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

The markers for the outyears 2013 and 2023 are based on a 25% average annual growth in production.
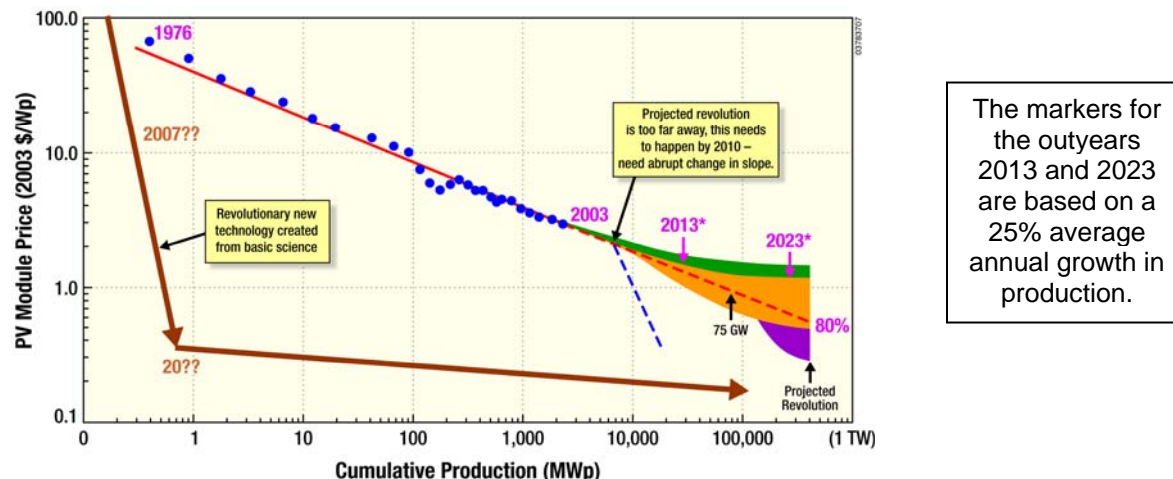
Figure 5 Learning curve for solar cells. The module price has been dropping 20% for every doubling of module production (80% learning curve) since 1976. Extrapolation of this historical trend into the future, plus a projected technological revolution at an annual production level of 150,000 MW$_p$, results in a prediction that \$0.40/W$_p$ would not be reached for another 20–25 yr. Reaching \$0.40/W$_p$ sooner to accelerate large-scale implementation of PV systems will require an intense effort in basic science to produce a technological revolution that leads to new, as-yet-unknown technology. This revolution requires a major reduction in the ratio of the PV module cost per unit area to the cell efficiency.

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

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

Needs of Direct-gap, Thin-film Photovoltaic Technologies. A second strategy for reducing costs is to use thin-film materials that have a very high absorptivity for solar photons. Such materials are called direct-band-gap semiconductors; Si is an indirect-band-gap semiconductor and absorbs relatively weakly, thus requiring a relatively large thickness of Si in the PV cell to absorb all the incident sunlight. Substantial research efforts have produced direct-band-gap CdTe and $CuInSe_2$ solar cells with efficiencies approaching 20%. Industrial efforts to manufacture cells made of these materials in high volumes are beginning to demonstrate success. However, this process has been slower than expected because much of the basic science of these solar cells is not understood. These polycrystalline solar cells are affected by many things, including the grain structure obtained for growth on foreign substrates, the effects of intentional and unintentional impurities on doping and performance (e.g., injection of sodium affects the performance of $CuInSe_2$ cells), and the nature of the active junction and ohmic contacts formed by poorly understood processes. A basic understanding of these issues would facilitate the technology transfer to large-scale production, enabling a revolutionary growth of the PV industry.

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

(1) An efficiency of 37.9% has been obtained, with possible pathways to higher efficiencies.

(2) Lattice mismatched III-V solar cells with performance approaching the radiative limit have been demonstrated, implying that such cells may reach efficiencies in the 40–50% range.

(3) A 1-kW multi-junction concentrator system is now supplying electricity to the grid, paving the way for larger prototypes and manufacturing; and

(4) In 2004, installations with sizes >100 kW increased to 20 MW, implying that a market appropriate for concentrators may be emerging.

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

Need for Revolution to Create New Technologies

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

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

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

Inorganic Photovoltaics

As shown in Figure 2, single-crystal Si solar cells, defined as Generation I cells, have module efficiencies of about 10–12% — leading to module costs of about $3.50/$W_p$. In order to lower the areal cost, Generation II approaches to PV systems involve the use of semiconductor thin films (amorphous Si, polycrystalline CdTe and $CuInSe_2$, dye cells, and organic PV cells). However, the system cost will be limited by BOS costs, which means that the Generation II systems cannot have arbitrarily low efficiency even if the module costs are negligible. With low areal costs for both modules and BOS of $75/$m^2$ each, 10% efficiency for Generation II modules (17% cell efficiency) would yield PV costs of $1.50/$W_p$ ($0.075/kWh). Thus, unless the module and BOS costs can be reduced well beyond the aggressive target of $75/$m^2$ each, achieving the goal of $0.40/$W_p$ ($0.02/kWh) will require efficiency and system costs per unit area that lie in the Generation III area of Figure 2.

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

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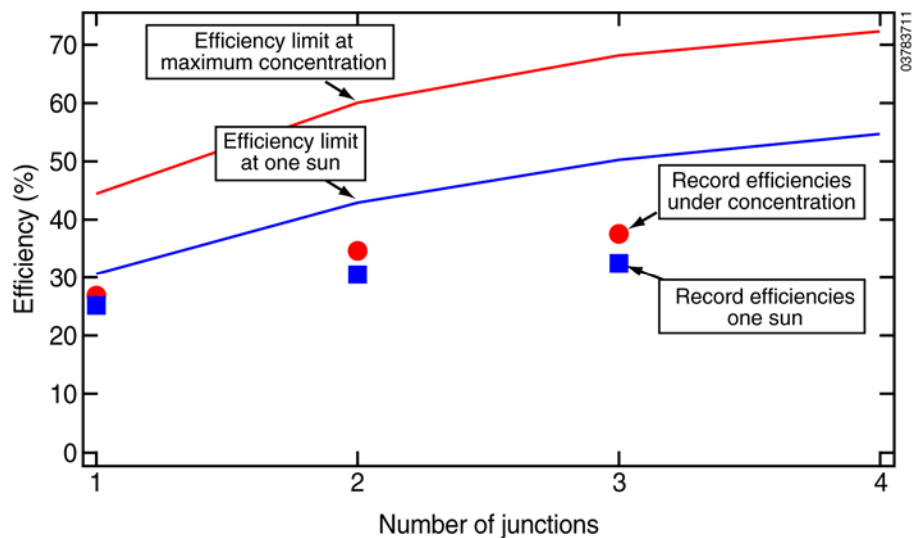
Figure 6 Current record efficiencies (as a function of the number of junctions) compared with the theoretical limits as predicted by the detailed balance analysis

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

Organic Photovoltaics

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

INORGANIC PV CELLS

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

The figure shows a conventional single p-n junction inorganic PV cell.
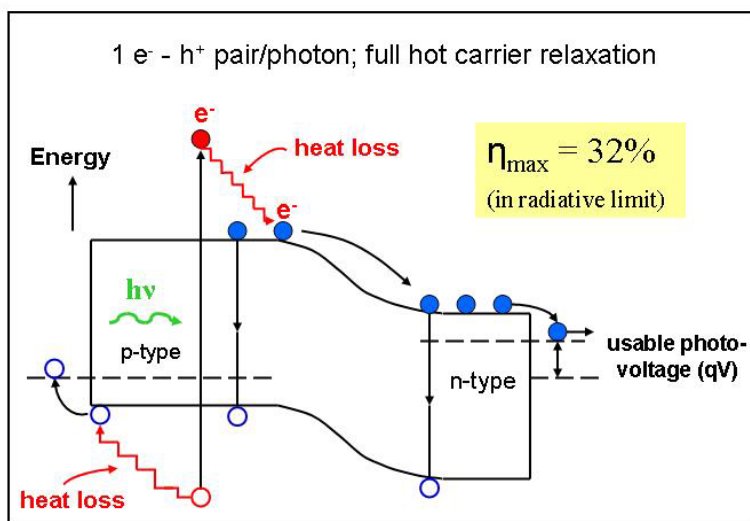
The basic principle of operation in an organic PV cell is that illumination of a mixture of electron-rich (donor) and electron-poor (acceptor) species leads to separation of (+) and (-) charge carriers. Collection of these carriers at electrodes produces an electrical current that can do work on a load in an external circuit. Although the basic principles behind the operation of organic PV cells and conventional p-n junction cells are similar, the details of key events, such as charge carrier generation and charge transport, are very different in the organic cells. Consequently, the basic understanding of the physics and chemistry of organic PV systems lags behind that of conventional p-n junction
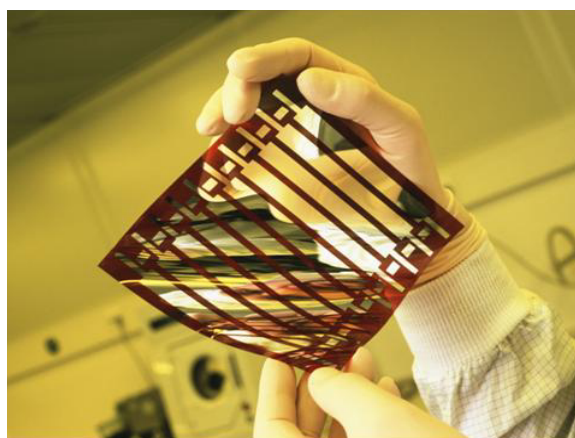
Figure 7 Flexible, plastic PV cell

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

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

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

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

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

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

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

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

(1) A device architecture designed to match individual solar photons, such as the tandem solar cell (see Figure 8);

(2) Up-conversion or down-conversion of the solar photons to match an existing single-junction PV design (see Figure 9).

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

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

Photoelectrochemistry

Photoelectrochemical (PEC) systems provide the best-known wet chemical method of converting sunlight into electrical energy or chemical fuels. PEC systems developed during the mid-1970s and 1980s for capture and conversion of solar energy into electricity and fuels are based on a semiconductor electrode in contact with an electrolyte solution (Memming 2001; Bard et al. 2002; Nozik and Memming 1996; Nozik 1978; Grätzel 2001). The solid-liquid configuration offers the following four advantages: (1) the junction required for efficient charge separation of photogenerated electrons and holes is very easily formed by simply immersing the semiconductor in an appropriate electrolyte solution; (2) the liquid electrolyte offers the capability of a readily conformable and strain-free junction; (3) a third electrode can be added to PEC cells to provide in-situ chemical storage for 24-hr/day power; and (4) the conversion of
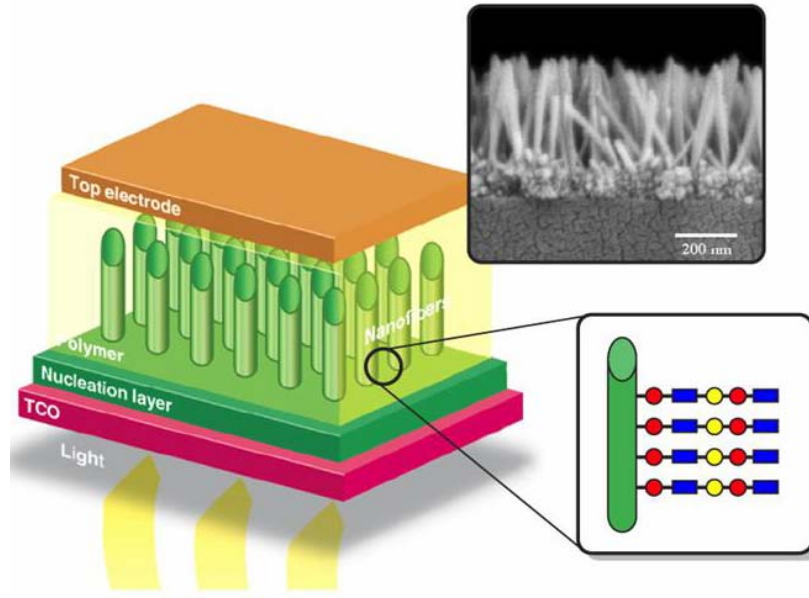
Figure 8 Structure for high-efficiency (50%) organic PV cell based on a nanostructured substrate onto which thin layers of molecular multi-junctions are grown and anchored onto the nanostructure surface. The red circle denotes an electron acceptor; the blue square, an electron donor; and the yellow circle, a metal nanoparticle.
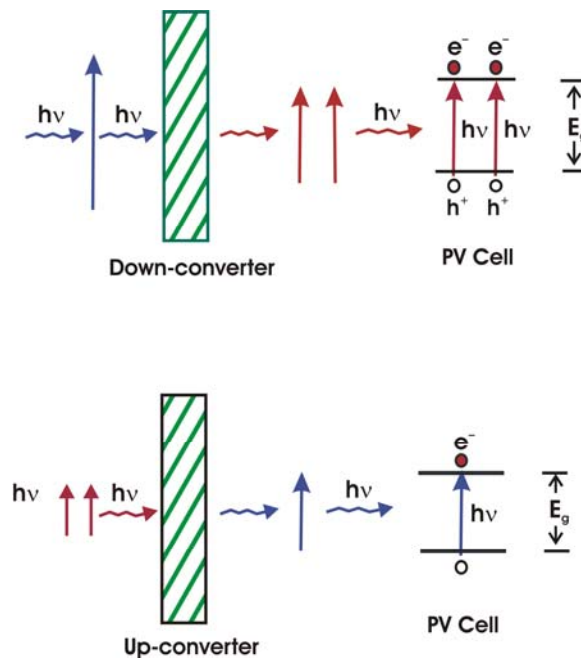
Figure 9 Down-conversion of incident solar photons splits the energy of high-energy photons into two photons of lower energy that can then be absorbed in the PV device more closely matched to the band gap energy and thus avoid thermalization (i.e., heating) losses. Up-conversion adds the energies of two lower-energy incident photons that otherwise would pass through the PV device to produce a single, higher-energy photon that is equal to or greater than the band gap and can therefore be absorbed.

ORGANIC PV CELLS

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

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

Organic Solar Cell (OSC)

OSC2 "p-type"
OSC1 "n-type"
metal 1 contact M1
metal 2 contact M2
e⁻
h⁺
hv
hv
exciton energy in OSC1 (optical bandgap)
exciton energy in OSC2 (optical bandgap)
electrical bandgap
Effective heterojunction bandgap, $E_{bg,hj}$
exciton binding energy

Perylene pyridylethylimide

Titanylphthalocyanine

Organic Solar Cell (with polymers)

PCBM blended with: OC_1C_{10}-PPV   P3HT

J_{SC} = 5.3 mA/cm²
V_{OC} = 0.82 V
FF = 61%
η = 2.5%

J_{SC} = 9.3 mA/cm²
V_{OC} = 0.56 V
FF = 60%
η = 3.5%

(under AM1.5 illumination)

TCO conducting polymer
polymer / fullerene blend
Al

SMU
Aluminum
LiF
Active layer
PEDOT:PSS
ITO
Glass

---

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

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

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

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

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

PHOTOELECTROCHEMICAL SOLAR CELLS

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

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

Electrochemical Solar Cell
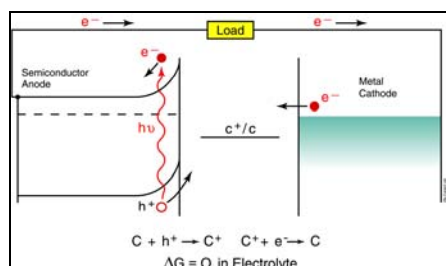
Dye-sensitized Nanocrystalline Solar Cell
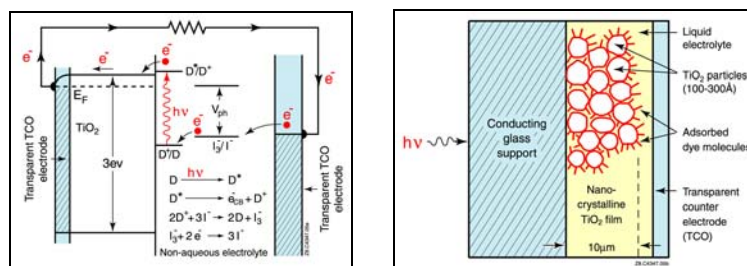
PHOTOELECTROCHEMICAL STORAGE CELLS

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

PEC Cell for Fuel Production: Photoelectrolysis of Water

EPV CELL WITH ELECTRICAL STORAGE
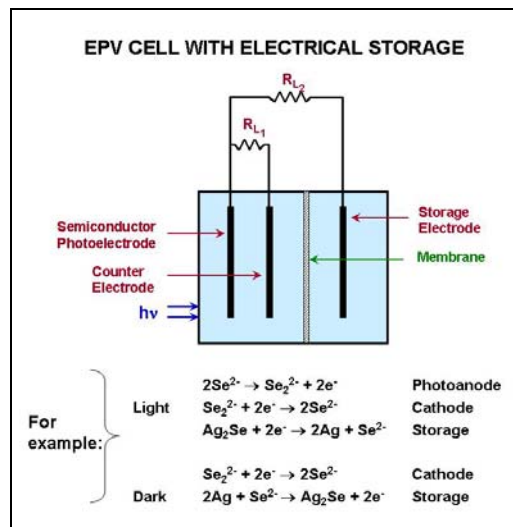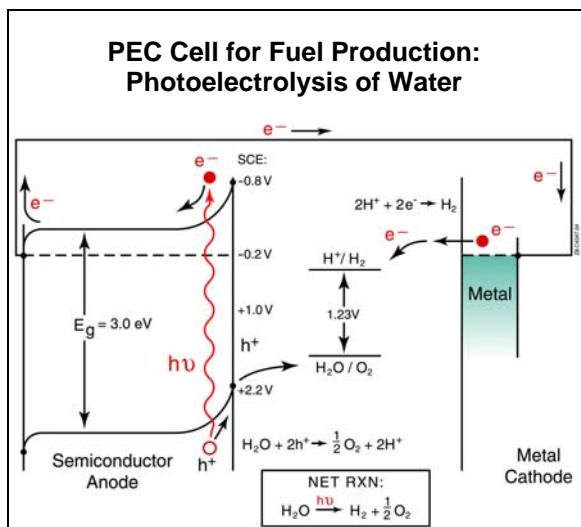
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BASIC RESEARCH CHALLENGES FOR SOLAR FUELS

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

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

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

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

(1) Use advances in biotechnology to genetically engineer plants to more efficiently — by a factor of 10 — harvest solar energy into biomass, so as to require less land area to produce the needed amount of stored biomass energy;

(2) Genetically engineer photosynthetic bacterial organisms to produce solar-derived fuels;

(3) Replicate the essential components of the machinery of photosynthesis outside of a natural organism or plant(i.e., in an artificial photosynthetic system) and obtain the needed ten- or hundred-fold efficiency improvement in a robust, cost-effective system;

(4) Construct entirely man-made chemical components (out of either organic or inorganic molecules or inorganic semiconductor particles) that, as an assembly, mimic photosynthesis by absorbing sunlight and converting the energy into chemical fuels such as CH_4 and H_2; the process developed must be efficient, robust, scaleable, and cost-effective.

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

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

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

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

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

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

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

CURRENT STATUS

Biomass-derived Fuels

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

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

ethanol selling price is $2.70/gal. To be cost effective in today's market, the overall cost of ethanol must be reduced by a factor of 3–5. The problem has been found to be more complex than simply finding new methods for cellulose-to-sugar conversion. Plants contain a wide variety of other molecules, whose structural relationships on the nanoscale are unknown. Understanding these relationships could lead to the development of cost-effective methods to break down cellulose and make the sugars available for bioconversion to fuels.
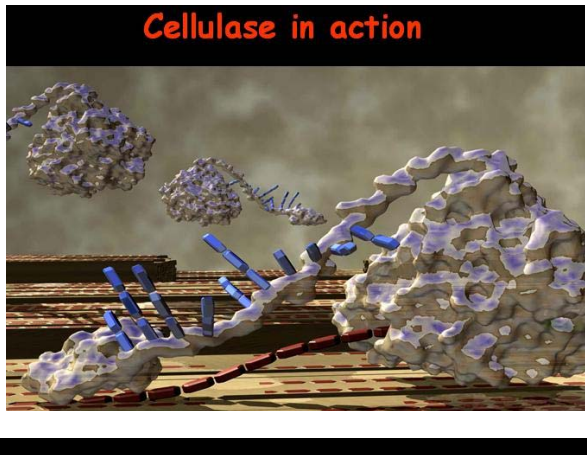
Cellulose is stable both chemically and biologically — a necessary feature in nature, where plants survive the elements for years. Work is underway to understand and develop molecular models of cellulose and the enzymes that hydrolyze it; however, that work has not moved from ideal systems (e.g., ones that do not involve the links to other plant structural components, such as hemicellulose and lignin) to those that are more realistic. The limitations to the rates at which enzymes break down cellulose are not understood either. If researchers could develop an understanding of those limitations, the rates could be increased, allowing shorter residence times and/or reduced enzyme loadings.

BIOMASS TO FUELS

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

Cellulase in action

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

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

convert it into H_2 and liquid fuels has also been achieved on a commercial scale. One of the issues preventing these processes from being economically viable is the rapid poisoning of the catalysts used in these processes.

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


Natural Photosynthetic Systems

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

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

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

# HOW DO PHOTOSYNTHETIC ORGANISMS CAPTURE LIGHT AND SEPARATE CHARGE?

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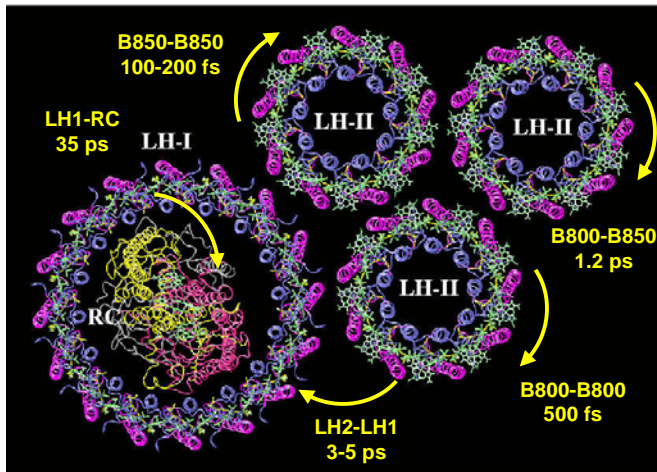
The image to the left shows the detailed molecular structures of the two light-harvesting proteins, LH1 and LH2, and the reaction center (RC) from a specific species of purple photosynthetic bacteria. The view is looking down onto the plane of the membrane in which these proteins reside. Green plant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

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

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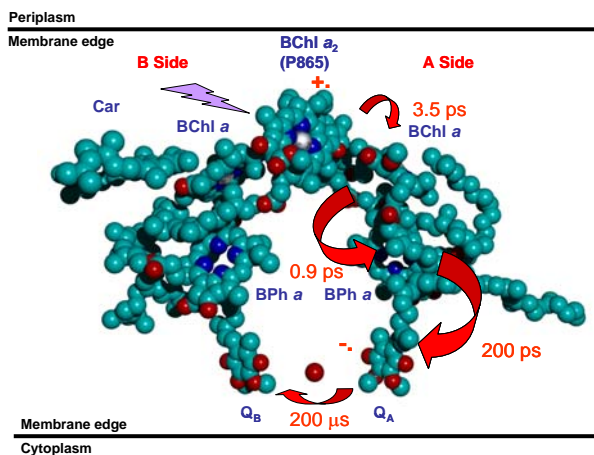
The image to the left shows a side-on view of the RC in the photosynthetic membrane. Only the cofactors responsible for photo-induced charge separation across the membrane are shown. Excitation of the bacteriochlorophyll dimer (BChl a_2) results in rapid electron transfer to an adjacent BChl a acceptor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

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

charge separation ensures highly efficient use of the photon energy, while the subsequent thermal steps move the charges ever-further apart to eliminate energy-wasting back reactions. The resulting separated charges live long enough to provide the energy necessary to drive the metabolic processes of the bacteria (Blankenship 2002; Woodbury and Allen 1995).

Photosystem I and II in Green Plants and Cyanobacteria. Photosystem I (PSI) functions to provide the chemical reducing agents that fix CO_2 in the form of carbohydrates. An x-ray structure of PSI, obtained at 2.5-Å resolution, shows that the PSI core is a large pigment-protein complex (Grotjohann et al. 2004). The largest two subunits bind the majority of the RC and core antenna pigments. Once again, these proteins display a symmetric structure analogous to that found in the RC from purple bacteria. While the active components of PSI are chemically different from those of purple bacteria, the central paradigm — light-harvesting energy transfer from the antenna to a chlorophyll-based primary electron donor in the RC, photoinduced charge separation, and several subsequent thermal electron transfer steps — is maintained. The overall complexity of PSI, as indicated by the number and nature of the molecular species participating in the overall process, is much higher than that exhibited by the purple bacteria.

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

PHOTOSYSTEM II: USING LIGHT TO SPLIT WATER

$$2H_2O \xrightarrow{4\ h\nu} O_2 + 4H^+ + 4e$$

Photo-induced charge separation within PSII creates a chlorophyll species called $P680^+$, one of the most powerful oxidants known in biology. $P680^+$ provides the oxidizing power to split water into O_2 and H^+ in the Mn-containing, oxygen-evolving complex (OEC) within the protein. The structure of the OEC is shown in detail above. The OEC contains one Ca and four Mn atoms, along with bridging oxygen atoms between them. The OEC splits water by losing four electrons, one at a time. These oxidative equivalents are accumulated following sequential absorption of single photons by the primary electron donor (P680) and subsequent charge separation: $P680 + Chl \rightarrow P680^+ + Chl^-$, where Chl is a nearby chlorophyll electron acceptor. Understanding the overall coupling between photo-induced electron transfer within PSII and the functioning of the OEC is essential to developing bio-inspired systems for fuels production, because efficient water splitting, coupled to catalytic reduction of H^+ to H_2, is one of the most important routes to clean solar fuels.

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

Bio-inspired Approaches to Photochemical Energy Conversion

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

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

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

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

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

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

DESIGNING AN ARTIFICIAL REACTION CENTER

## Efficient Photoinduced Charge Separation

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

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

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

Electron Transfer Rate vs. Free Energy of Reaction
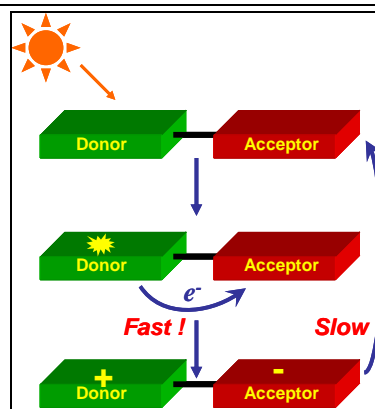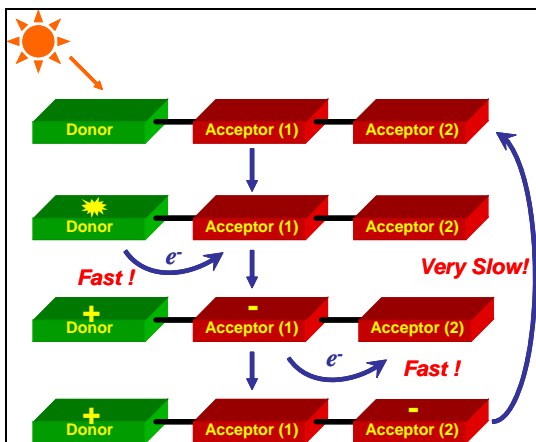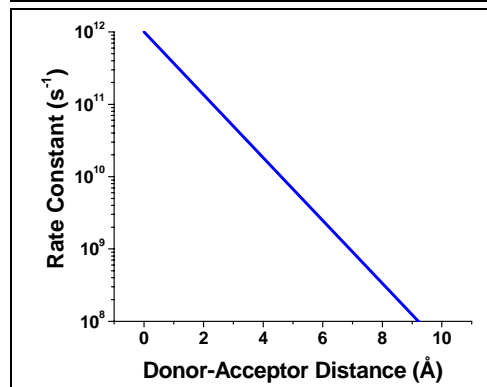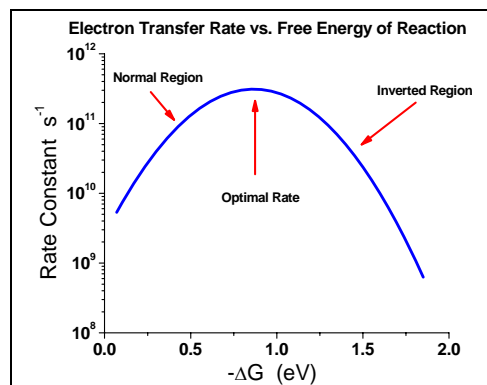
**Carotene-Porphyrin-Fullerene Triad**
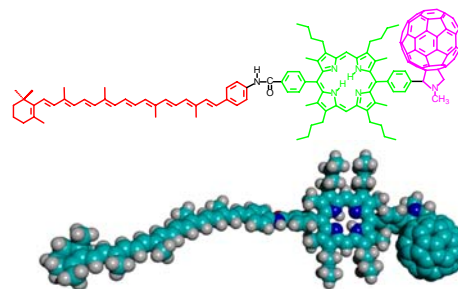
artificial RCs, have proven to be important tools to directly gauge the magnitude of the intermolecular interactions responsible for a given rate of electron transfer and determine how this rate depends on the details of molecular structure.

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

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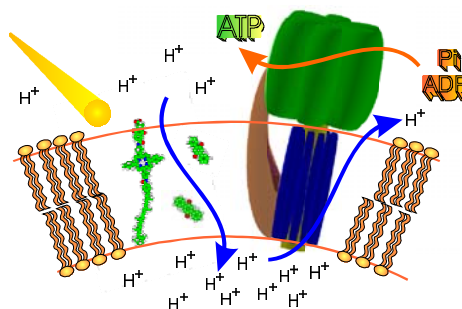
Figure 10 Hybrid light-driven proton pump using charge separation within a donor-acceptor triad and ATP synthase incorporated into a liposome (Source: Steinberg-Yfrach et al. 1998)

Photocatalysis and Photodriven Reactions

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

reactions must produce the desired fuel (e.g., H_2, CH_3OH) and a desirable co-product (e.g. O_2 from water oxidation). In so-called heterogeneous (insoluble) catalysts, requirements (1) and (2) are usually implemented by using semiconductor assemblies, while in homogeneous (soluble) catalysts these functions are performed by using molecular assemblies in solution. The critical issue for requirement (3) is the coupling of the one-photon light absorption events in (1) and (2) to the proton-coupled, multi-electron processes required for catalysis. Most previous efforts have used catalysts driven by one-electron reactions to avoid high-energy intermediates. However, fuel production requires multi-electron oxidation and reduction reactions, so new catalysts that couple single-photon events to the accumulation of multiple redox equivalents are essential.
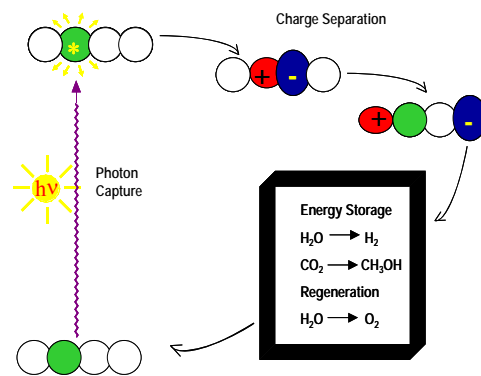
Figure 11 Solar production of fuels by the following sequence: (1) light absorption, (2) charge separation, and (3) use of the separated charges to produce fuel (e.g., H_2, CH_3OH) and co-product (e.g., O_2 from water oxidation). The reactions shown in the black box require efficient catalysts.

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

Homogeneous Photocatalytic CO$_2$ Reduction. Most systems studied to date generally use transition metal complexes (e.g., containing Ru and Ir) as catalysts for photoreduction of CO_2 because they absorb a significant part of the solar spectrum, have long-lived excited states (about 1 μs), and can transfer electrons to or from small molecules. Typical systems also include a secondary metal complex (e.g., containing Co) as a co-catalyst to carry out the reduction of CO_2. Metal hydride complexes are also important because bimolecular reactions of hydrides or their reactions with H_2O/H_3O^+ are responsible for the formation of H_2. While both metal hydride and metal-CO_2 complexes pertinent to some of the systems are known, in no case has the reduction mechanism been completely determined. For example, the best systems reported thus far show quantum efficiencies as high as 38% using a Re sensitizer, but have disappointing turnover frequencies of CO formation of <10/h.

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

CATALYSTS FOR CO₂ REDUCTION

Photo-driven catalysts for CO_2 reduction have made use of the versatile photochemistry and redox properties of Ru complexes. Photo-excitation of $Ru(bpy)_3^{2+}$ (below, top panel) results in formation of an excited state that reacts readily with the sacrificial donor triethanolamine. The reduced $Ru(bpy)_3^+$ can then act as a source of electrons to drive a catalytic cycle of the type shown in the bottom panel below (Pugh et al. 1991). In this cycle, another Ru complex catalyzes the reduction of CO_2 to formate ion. Input of electrons is required at two points in the overall cycle. The overall mechanism for the catalytic reduction of CO_2 is complex, so that a great deal of work remains to find optimal catalysts that are well-coupled to the photochemical agents that use solar energy to provide a source of electrons to drive the catalysts.
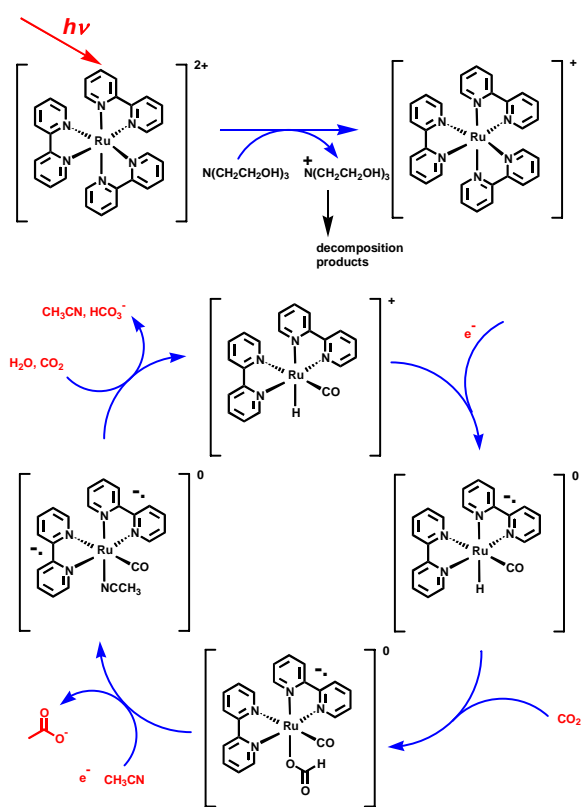
CATALYSTS FOR WATER OXIDATION

Catalysts with sufficient oxidizing power to split water remain relatively rare. Yet, several recent catalysts based on Mn and Ru have demonstrated water oxidation following addition of strong oxidants to access the higher oxidation states of these metals. As an example, the top panel shows the structure of a Mn_2 complex that generates O_2 obtained from water using NaOCl as an added oxidant (Limberg et al. 1999). The mechanism of catalysis is shown in the lower panel. Thus far, the turnover frequencies and the stability of water oxidation catalysts remain low. In addition, coupling of a photo-driven oxidant to these catalysts has not been accomplished.
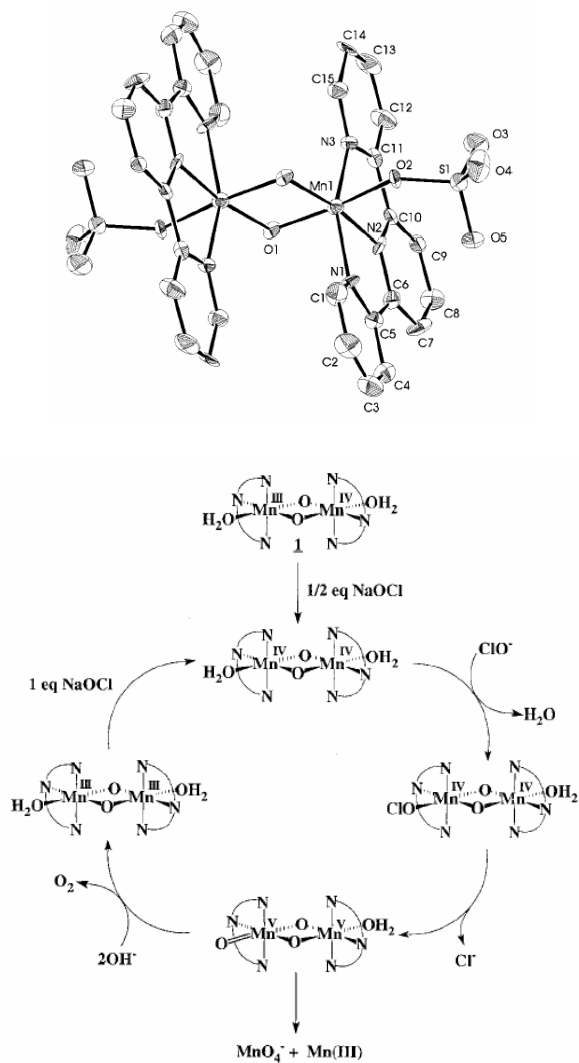
Nocera 2001). All water oxidation catalysts examined to date are based on transition metals that have oxidation states accessible in the 1–1.5 V range. Standing alone among these catalysts is the water oxidation enzyme of PSII in green plants. In its OEC, the enzyme contains a Mn cluster, which is capable of turning over about 10^3 O_2 molecules/s (see *Photosystem II, Using Light to Split Water* sidebar) (Ferreira et al. 2004; Rüettinger and Dismukes 1997). Wh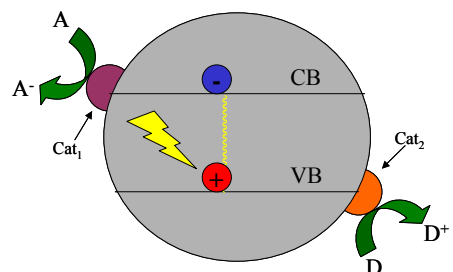ile several transition-metal complexes have been shown to catalyze water oxidation, turnover frequencies remain disappointingly low.

Heterogeneous Semiconductor-based Photocatalysis. In 1972, Fujishima and Honda reported the first complete water photoelectrolysis system (Fujishima and Honda 1972). It was based on an *n*-TiO$_2$ anode with a small electrical bias to compensate for the insufficient reducing power of electrons in the conduction band of TiO$_2$ to drive the cathodic water reduction reaction. The requirements for an effective photocatalytic semiconductor are dictated by the positioning of the valence and conduction bands and by chemical stability during the catalytic cycle. In the case of reactions to produce H$_2$ and O$_2$, the conduction band must be above 0 V vs. normal hydrogen electrode (NHE) to produce H$_2$, and the valence band must be below +1.2 V vs. NHE to produce O$_2$ (Grätzel 1983). Soon after, *n*-SrTiO$_3$, for which the conduction band is higher in energy than that of TiO$_2$, was used without an electrical bias (Wrighton et al. 1976). In 1979, photoelectrocatalytic reduction of CO$_2$ in aqueous suspensions of semiconductor powders was first accomplished (Inoue et al. 1979).

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

Figure 12 Schematic diagram of photoredox processes at a semiconductor particle

electron-hole formation. Bulk semiconductors offer poor quantum conversion efficiencies (0.1–0.01%) because of low surface areas and significant charge recombination (Grätzel 1983). The development of high-surface-area semiconductor dispersions and porous thin films has greatly improved the capabilities of semiconductor-based photocatalysts. Semiconductor catalytic dispersions have been made with both solid (e.g., polymers) and liquid (e.g., colloids) supports and can be used to catalyze transformations on both liquid and gaseous substrates.

Semiconductor particle photocatalysis has been the most studied heterogeneous approach to H$_2$ production (Linsebigler et al. 1995; Kudo et al. 2004). Colloids or nanoparticles offer several advantages over bulk catalysts by having high electron-hole pair separation efficiencies (~100%), large interfacial surface areas, and short electron-hole diffusion lengths to the interface; in addition, they are readily studied by using spectroscopic techniques (Grätzel 1983).

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

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

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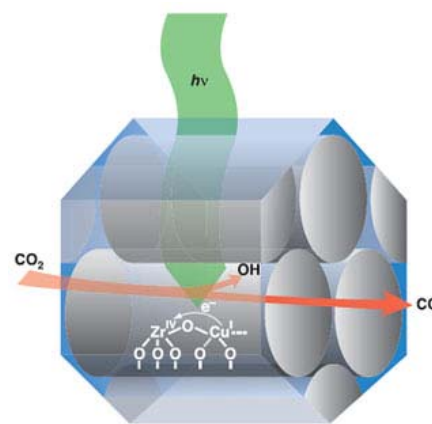
Figure 13 Zr and Cu redox sites on a nanoporous inorganic support carry out the stepwise conversion of CO_2 and water via CO to fuels using visible light in a solvent-free system.

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

Biomass-derived Fuels

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

Natural Photosynthetic Systems

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

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

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

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

Catalytic power and specificity, which are key attributes of enzyme-mediated catalysis, have their origins in the active environment provided by the protein. The same is true in the primary solar energy conversion reactions of photosynthesis. The proteins involved in the light-harvesting complexes and the RCs are not just inert scaffolds. They provide much more than just a means of optimally positioning the chromophores and the electron transfer cofactors. The medium provided by the protein actively promotes, enhances, and indeed controls the light-harvesting and electron-transfer reactions both within the protein and across interfacial protein boundaries. This is a key feature of the natural system that allows it to operate so efficiently. Furthermore, proteins can be readily engineered, via genetic modification, to explore a diversity of structure/function scenarios. Because of major limitations imposed by covalent synthesis of large assemblies, construction of the next generation of bio-inspired solar-energy conversion devices will require placing the chromophores into a "smart matrix" to control their key electronic properties by using weak interactions and self-assembly. Achieving efficient integrated solar energy conversion systems using smart matrices will require the following: (1) learning how natural protein matrices control and optimize energy and charge transport both within a single protein and between proteins; (2) engineering proteins, polymers, membranes, gels, and other ordered molecules to provide tailored active environments (i.e. smart matrices); (3) incorporating bio-inspired cofactors within the designed matrix; (4) integrating multiple cofactor-matrix assemblies to perform the overall function; (5) characterizing the coupling between the cofactors and the matrix in natural and bio-inspired systems by using advanced techniques; and (6) developing smart matrices that compartmentalize incompatible products (e.g., O_2 and H_2).

Bio-inspired Approaches to Photochemical Energy Conversion

A major scientific challenge is the preparation of bio-inspired, molecular assemblies that integrate light absorption, photoinduced charge separation, and catalytic water oxidation/fuel formation into a single unit. These integrated assemblies must take full advantage of both molecular and supramolecular organization to collect light energy and transfer the resulting excitation to artificial RCs. These centers must separate charge and inject electrons and holes into charge transport structures that deliver the oxidizing and reducing equivalents to catalytic sites where water oxidation and CO_2 reduction occur. It is critical to understand how excitation energy flow from the antenna to a RC depends on molecular structure. In addition, charge transport structures for delivery of redox equivalents to catalysts must be developed. By analogy to natural photosynthesis, it is important to provide control elements, or "throttles," to optimize energy and charge flow within an artificial photosynthetic system as it responds to varying light intensities and spectral distributions. One of the most difficult tasks critical to achieving system integration is coupling single-photon events to the accumulation of multiple-redox equivalents necessary to drive multi-electron, fuel-forming chemistry within a catalyst.

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

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

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

Photocatalysis and Photodriven Reactions

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

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

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

CONCLUSION

The efficient production of clean solar fuels presents many scientific challenges. Yet progress in this field to date provides a strong argument that this goal is achievable. The major scientific challenges that will need to be addressed are (1) understanding biological mechanisms for the efficient production of fuels from biomass; (2) developing a detailed knowledge of how the molecular machinery of photosynthesis captures and converts sunlight into chemical energy; (3) discovering how to use this knowledge to develop robust, bio-inspired chemical systems to carry out photoconversion; (4) developing catalysts that use photo-generated chemical energy to efficiently produce such fuels as CH_4 and H_2; and (5) developing an integrated photo-driven system for solar fuels formation with optimized performance and a long functional lifetime.

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BASIC RESEARCH CHALLENGES FOR SOLAR THERMAL UTILIZATION

CURRENT STATUS

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

High-temperature Solar Thermal Systems

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

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

Solar Concentrators

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

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

THREE TYPES OF CONCENTRATED SOLAR "THERMAL" SYSTEMS

direct & diffused sunlight

process heat

hot water

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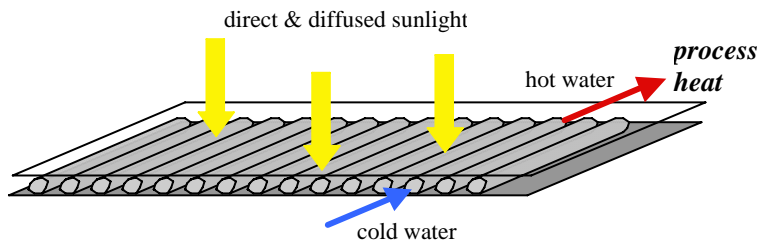
Low-temperature solar thermal systems. This system does not involve sunlight concentration, or occasionally may employ low-concentration (C ≤ 2). This system is suitable for home use where it usually heats hot water for direct use or home heating.

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

photovoltaic power conversion

electricity

direct sunlight

concentrated sunlight

optical concentrator

solar to thermal power conversion

heat to electricity or heat to chemical potential power conversion

hot output

cold input

direct sunlight

concentrated sunlight

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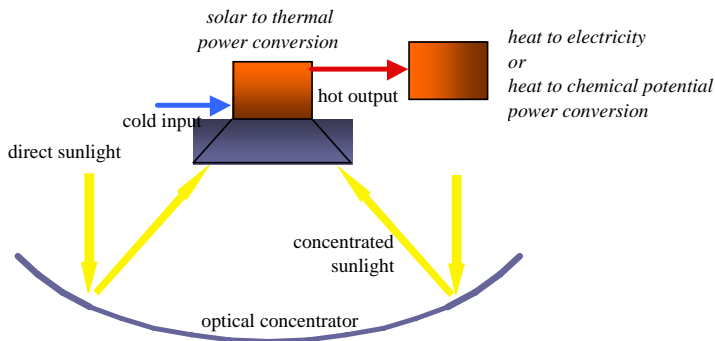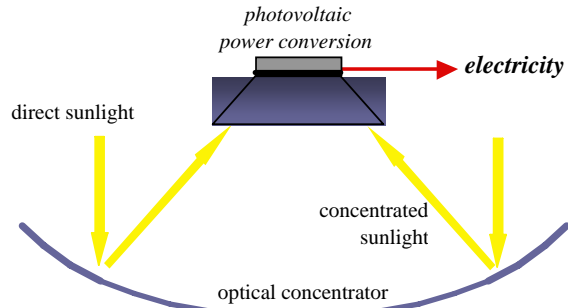
High-temperature solar thermal systems. Such systems require optical concentration of direct sunlight at a ratio varying from about 20 to several thousands, depending on the specific process and system involved. Concentrated solar thermal systems are large megawatt(electric) systems that can be used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

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

Two 10-MWe facilities are situated in the United States near Barstow, California, and one 2.5-MWe facility is in Almaria, Spain. Present estimates of large-scale (>50-MW) facility costs are about $3/W (Sargent & Lundy 2003; Stoddard et al. 2005). A recent study (Pitz-Paal et al. 2005) indicates that the new developments discussed here should lead to a cost reduction of at least $0.5/W. Materials development aimed at high-temperature performance would impact efficiency.
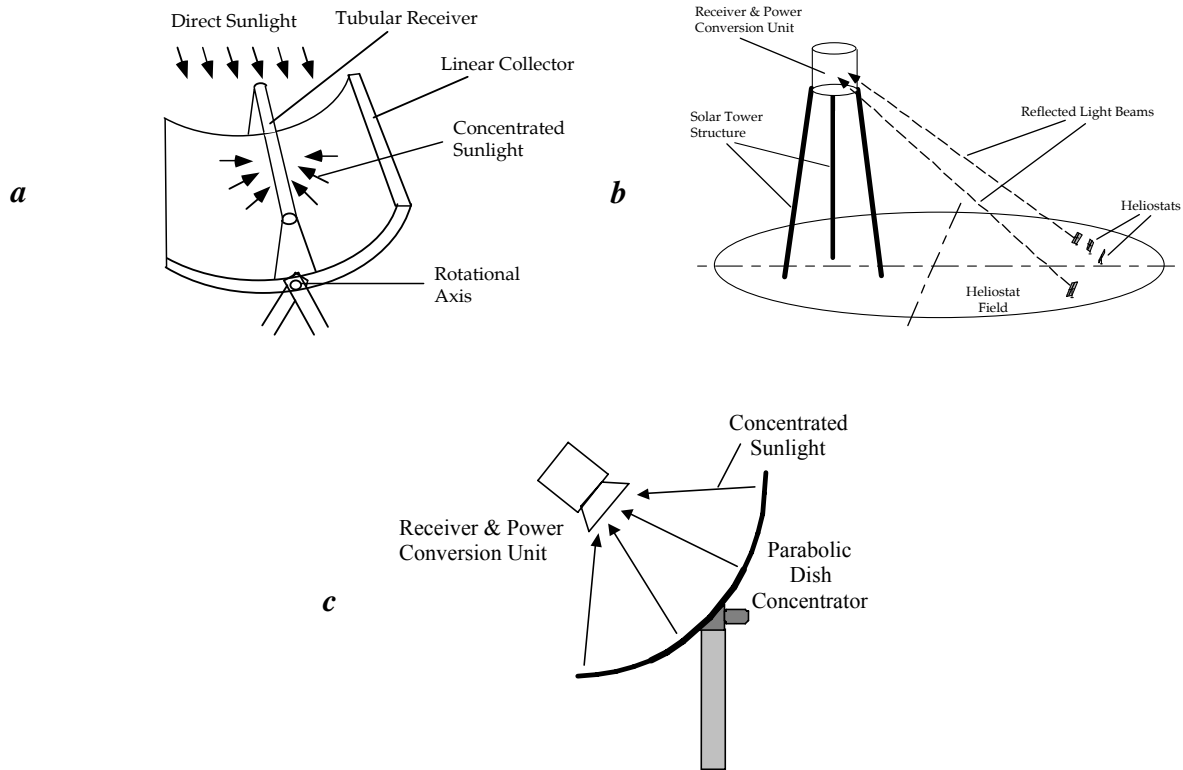
Figure 14 Three types of solar concentrators utilizing (a) linear collectors that focus on tubular receiver, (b) central receiver (solar power tower) with heliostat field that tracks the sun, and (c) on-axis tracking system with parabolic dish concentrator

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

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

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

Solar Thermal to Electric Energy Conversion

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

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

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

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

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

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

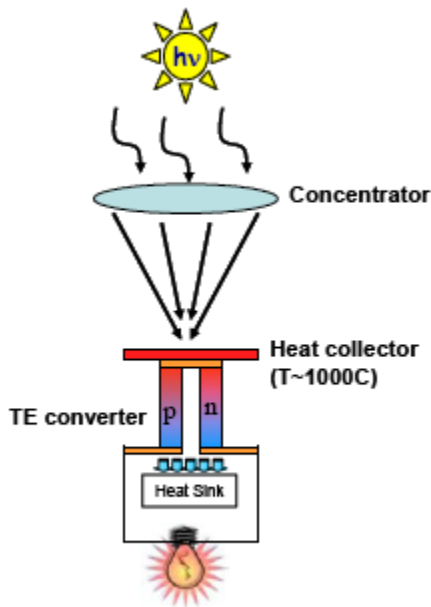A thermoelectric power generator has a maximum efficiency given by

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

where

T_h, T_c = temperatures at the hot and cold sides

THERMOELECTRIC MATERIALS AND DEVICES

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

Figure 1 Illustration of a solar-thermoelectric power generator.
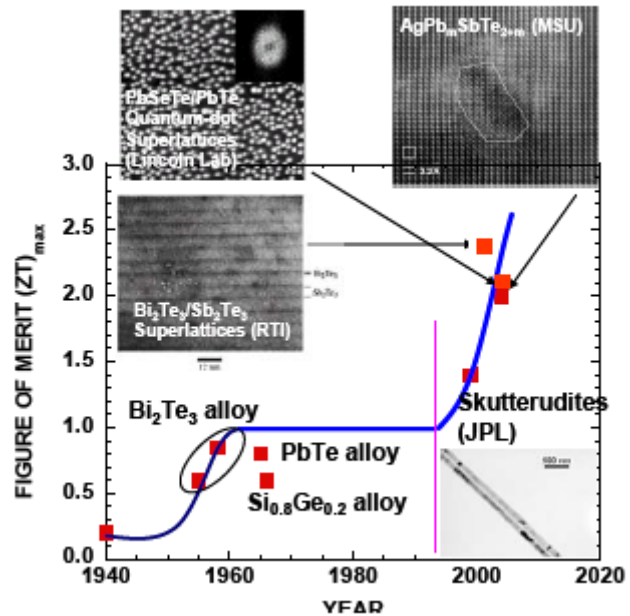
Figure 2 Progress timeline in thermoelectric materials.

T_m = mean temperature

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

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

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

Commercial thermoelectric materials, with a maximum ZT~1, were mostly discovered in 1950s. Little progress was made in the subsequent years. In the 1990s, the possibility of improving the thermoelectric figure of merit based on electron band gap engineering and phonon engineering in nanostructures was investigated (Hicks and Dresselhaus 1993). These ideas have lead to a resurgence in thermoelectric research and significant progress in improving ZT, particularly based on nanostructured materials (Tritt 2001; Chen et al. 2003). Venkatasubramanian et al. (2001) reported that Bi_2Te_3/Sb_2Te_3-based *p*-type superlattices have a room-temperature ZT of 2.4. Harman et al. (2002) reported that PbTe/PbTeSe superlattices with nanodots formed by strain have a room-temperature ZT of 2.0. Hsu et al. (2004) reported bulk nanostructures of $AgPb_2SbTe_{2+m}$. with a ZT of 2.2 at 527°C. Meanwhile, several research projects aiming at improving device efficiency based on more mature materials are under way. The Jet Propulsion Laboratory reported a segmented thermoelectric unicouple with an efficiency of ~14% with the hot side at 975K and cold side at 300K. Solar thermoelectric power generators made of materials with ZT~4 operating between room temperature and 1000°C would reach an efficiency of 35%. Given the impressive development made in the field of thermoelectrics over the past decade, the development of such materials seems to be a realizable goal.

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

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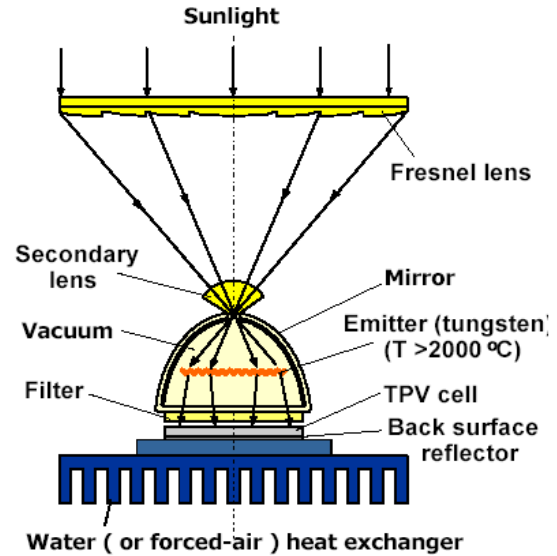
Figure 15 A possible set-up of a solar TPV system (courtesy: V.M. Andreev, IOFFE, St. Petersburg, Russia)

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

where

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

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

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

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

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

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

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

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

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

Concentrated Solar Thermochemical Processes

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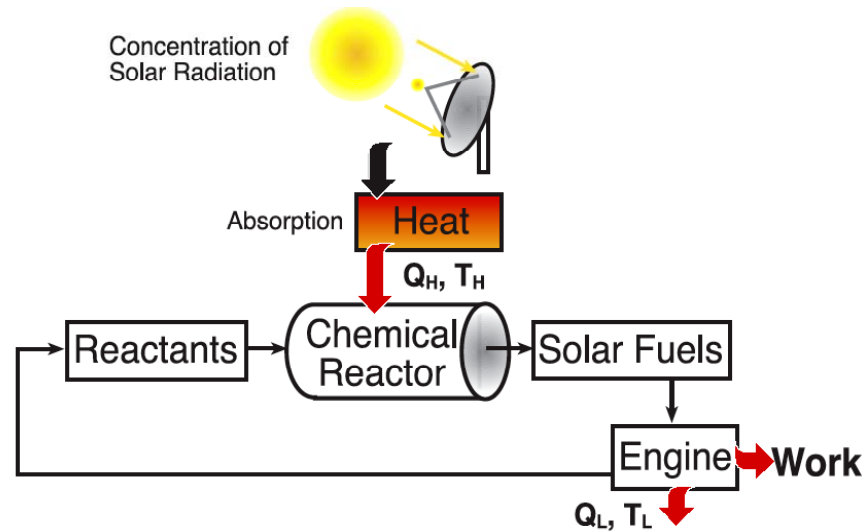
Figure 16 General concept of solar-driven thermochemical cycle

Water-splitting Thermochemical Cycles. In recent years, significant progress has been made in the development of optical systems for large-scale solar concentration capable of achieving mean solar concentration ratios exceeding 2,000 suns (1 sun = 1 kW/m^2), and present efforts are aimed at reaching concentrations of 5,000 suns. Such high radiation fluxes allow the conversion of solar energy to thermal reservoirs at 2000K and above, which are the conditions needed for efficient water-splitting thermochemical cycles using metal oxide redox reactions. This two-step cycle consists of first-step solar endothermic dissociation of a metal oxide and second-step nonsolar exothermic hydrolysis of the metal. The net reaction is $H_2O = H_2 + 0.5O_2$, but since H_2 and O_2 are formed in different steps, the need for high-temperature gas separation is thereby eliminated.

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

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

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

- Evaluation of novel processes for fuel synthesis (Möller et al. 2002; Dahl et al. 2004) and material production (Murray et al. 1995; Wieckert et al. 2004);

- Development of novel solar reactors (Anikeev et al. 1998; Osinga et al. 2004); and

- Catalyst development for solar-driven high-temperature gas-gas reactions (Berman and Epstein 1997).

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

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

Low-temperature Solar Thermal Systems

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

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

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

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

BASIC SCIENCE CHALLENGES, OPPORTUNITIES, AND RESEARCH NEEDS

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

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

Thermoelectric Materials

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

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

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

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

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

Nanoscale thermoelectric materials that can independently reduce phonon transport without deteriorating electronic transport have been implemented in Bi_2Te_3/Sb_2Te_3 superlattices (Ventakatasubramanian et al. 2001) offering ZT~2.4 at 300K and quantum dot PbTe/PbTeSe superlattices (Harman et al. 2002) offering ZT~2 at 550K. Most of the enhancements have been attributed to lattice thermal conductivity reduction in nanoscale dimensions. It is anticipated that further reduction is possible with a comprehensive understanding of phonon transport in low-dimensional systems. There is also potential for significant ZT enhancement through quantum-confinement effects (Hicks and Dresselhaus 1993).

Thermophotovoltaics

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

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

Key research needs are as follows:

- *Nanostructured metallic and dielectric materials with low diffusion and evaporation rates*: The major challenge of spectral control for TPV systems is given by the high operating temperatures of ~1,200°C in the case of fuel-powered TPV and ~2,000°C in the case of solar TPV. Diffusion processes and evaporation of material may limit the durability of the components significantly. Suitable concepts of material engineering to reduce 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. Currently, the techniques for producing nanostructures are top-down approaches that are limited to small homogeneously structured areas and to flat surfaces. They are also not cost-efficient. Thus, novel manufacturing techniques need to be developed, and these very likely will incorporate self-organization processes.

- *Novel device concepts*: Novel device concepts such as microgap TPV and device structures should be explored. Tunneling of evanescent and surface waves can lead to devices with higher power density and efficiency. Technological challenges to maintain the gap in the range of 10 nm to submicrons in high-temperature systems must be solved for such concepts to be useful in practical systems.

Solar Concentrators and Hot-water Heaters

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

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

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

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

Solar Thermochemical Fuel Production

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

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

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

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

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

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CROSS-CUTTING RESEARCH CHALLENGES

BACKGROUND

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

Low-dimensional Materials and Solar Energy

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

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

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

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

System Assembly and Defect Tolerance

To realize the potential of nanoscale-based solar conversion, the chemistry of molecular and material synthesis and assembly must be further elucidated. The synthesis of complex molecules, macromolecules, and nanoparticles is an underlying tool that continues to evolve in important ways. The key limiting issue now is the merging of these component building blocks into functional assemblies and, ultimately, into complete systems. This capability requires improved understanding of the organic-inorganic hard-soft interfaces, as well as the ability to harness multiple weak interactions to create designed patterns. This is how biological materials are organized on length

EFFECTS OF LOW DIMENSIONALITY

Reduced dimensionality can be used to control propagation and interactions of photons, electrons, and phonons.

Photon distributions are controlled in photonic crystals; the plot in "reciprocal space" shows the limited momentum and spatial direction that photons can have in controlled geometries.

The energy distribution of possible electronic energy levels is drastically affected by spatial confinement

scales larger than those of individual macromolecules, yet it remains very challenging for chemists and materials scientists working with artificial components. It is important for researchers to emulate many features of biological system assembly, chief among them (1) the ability to create advanced materials despite the presence of disorder and defects and (2) the ability not only to assemble components, but also to disassemble and reassemble them. These capabilities are essential for creating advanced solar converters that combine high performance with low cost.

New Experimental and Theoretical Tools

Progress in the field of solar energy depends critically on the development of new tools for the characterization of matter and on new theoretical tools. On the experimental front, one major goal is to create probes that can reveal the structure and composition of nanoscale materials with atomic resolution. A second goal involves development of tools that can be used to follow the complete flow of energy through each primary step of the solar conversion processes — from absorption, to charge transfer, transport, harvesting, and chemical conversion and separation. Theoretical tools are also needed to aid in the understanding of these elementary steps. The wide
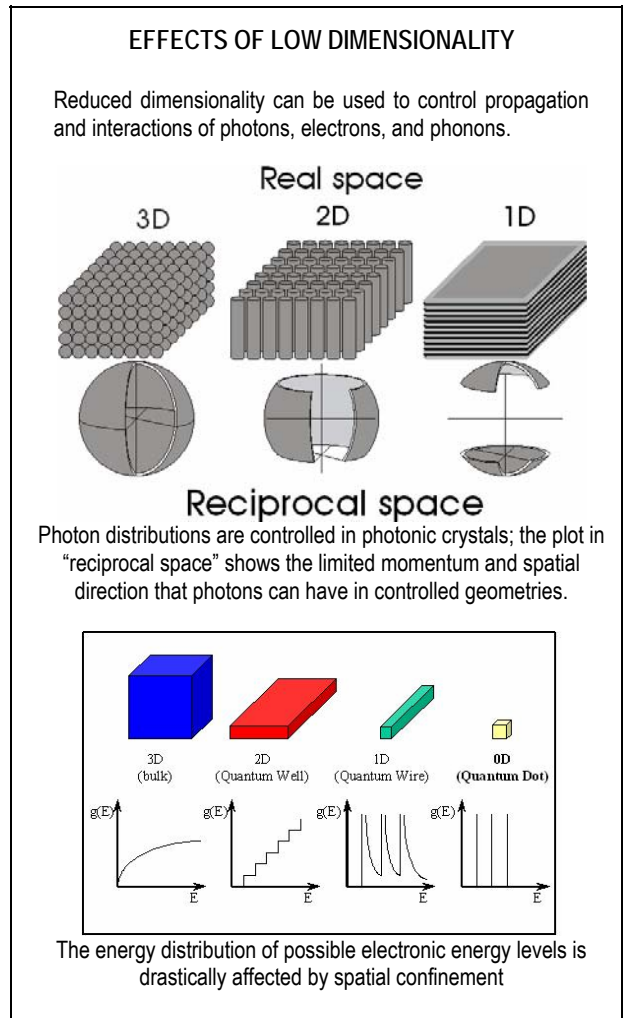
range of time and length scales spanned by these phenomena poses a significant theoretical challenge. The ability to compute the properties of systems with 1,000 to 10,000 atoms will permit modeling of complex problems, such as the electrochemical behavior of molecule-nanocrystal systems, catalytic hydrogen production, and biological light-harvesting systems. In addition, there is a significant need to create "inverse tools," which receive a wide range of simultaneous desired properties as inputs and yield materials arrangements as outputs.

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

ENHANCED PHOTON MANAGEMENT

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

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

Photon management might also take a biomimetic approach, for which the light-harvesting techniques found in natural systems provide guidance (Scholes 2003; Diner and Rappaport 2002; Chitnis 2001). Other areas in which new approaches might emerge include the use of materials exhibiting a negative index of refraction (Pendry 2000) or the use of highly scattering materials to localize photons (Ziegler 2003).
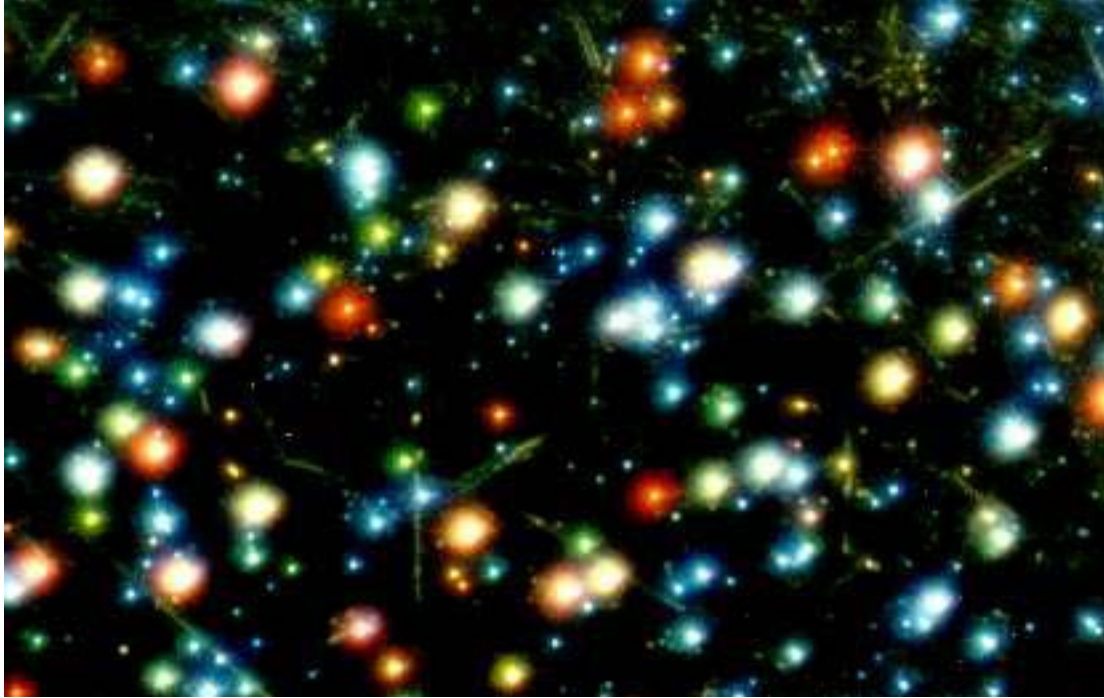
Figure 17 Control of light fields using metallic structures. Recent advances have permitted the concentration of light on a very fine length scale by using nanoscale structures. The figure shows an experimental image of white light scattering from silver nanoparticles. The color differences arise from the limits imposed by particle shape on the interactions of light and electrons within a nanoparticle. Enhancements in the light intensity exceeding 1,000 times can be achieved by using appropriately shaped nanostructures, as has been demonstrated by single-molecule Raman scattering and other enhanced optical effects. (Source: Michaels, Nirmal, and Brus 1999)

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

Research Issues

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

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

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

Impact

The primary processes of photon delivery, in terms of both spatial and spectral distribution, and optical absorption are common to all approaches to solar energy conversion. Advances in photon management and the tailoring of optical absorption properties can consequently impact the efficiency of any solar energy scheme.
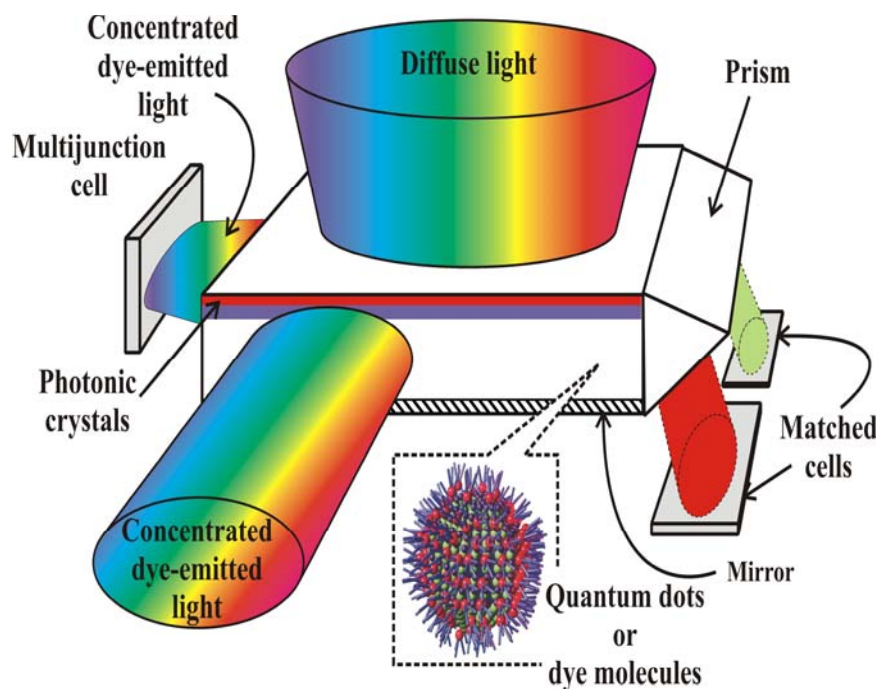
Figure 18 Concentration of sunlight provides significant advantages for many schemes of solar energy conversion. While traditional methods using mirrors have been developed, new approaches suitable for large areas are critical. The figure depicts a concentrator that makes use of photonic crystal filters (top of collector) and quantum dots or dye molecules (solution between plates) to achieve large-area light collection. (Source: FULLSPECTRUM undated)

CONTROL OF CARRIER EXCITATION, CHARGE TRANSPORT, AND ENERGY MIGRATION

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

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

Research Issues

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

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

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

Impact

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

INTERFACE SCIENCE OF PHOTO-DRIVEN SYSTEMS

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

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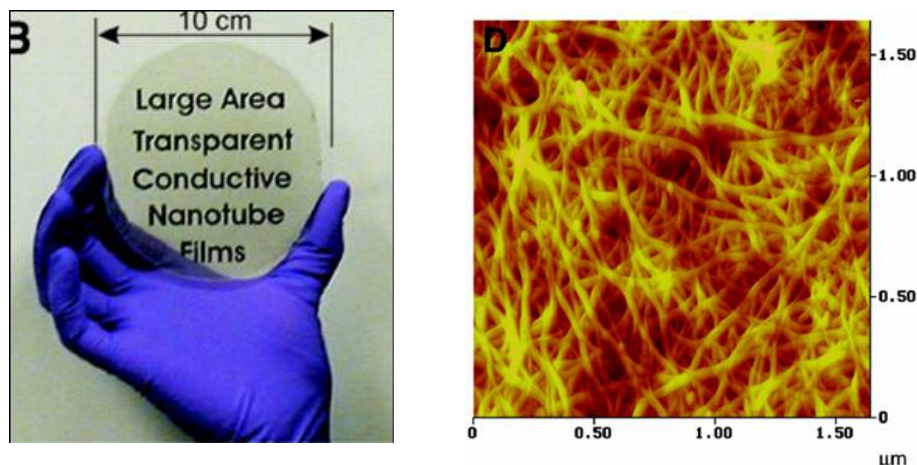
Figure 19 Transparent conductive electrodes represent one of the major challenges for PV devices. The problem involves both the bulk properties of the electrode material and its interface with the PV media. The figure shows the progress achieved in developing a new transparent conductive electrode material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

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

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

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

Research Issues

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

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

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

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

Impact

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

THERMAL STORAGE METHODS

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

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

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

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

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

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

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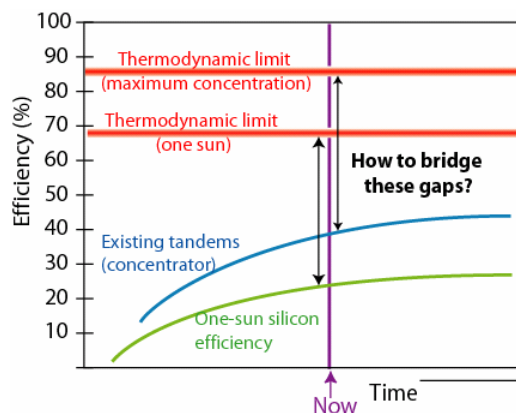
PRIORITY RESEARCH DIRECTIONS

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.
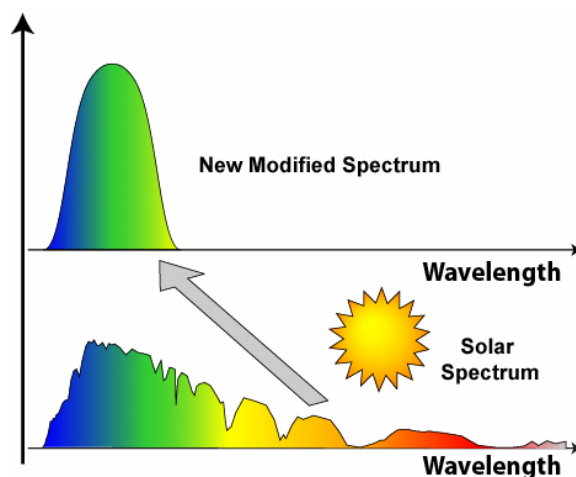
RESEARCH DIRECTIONS

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.
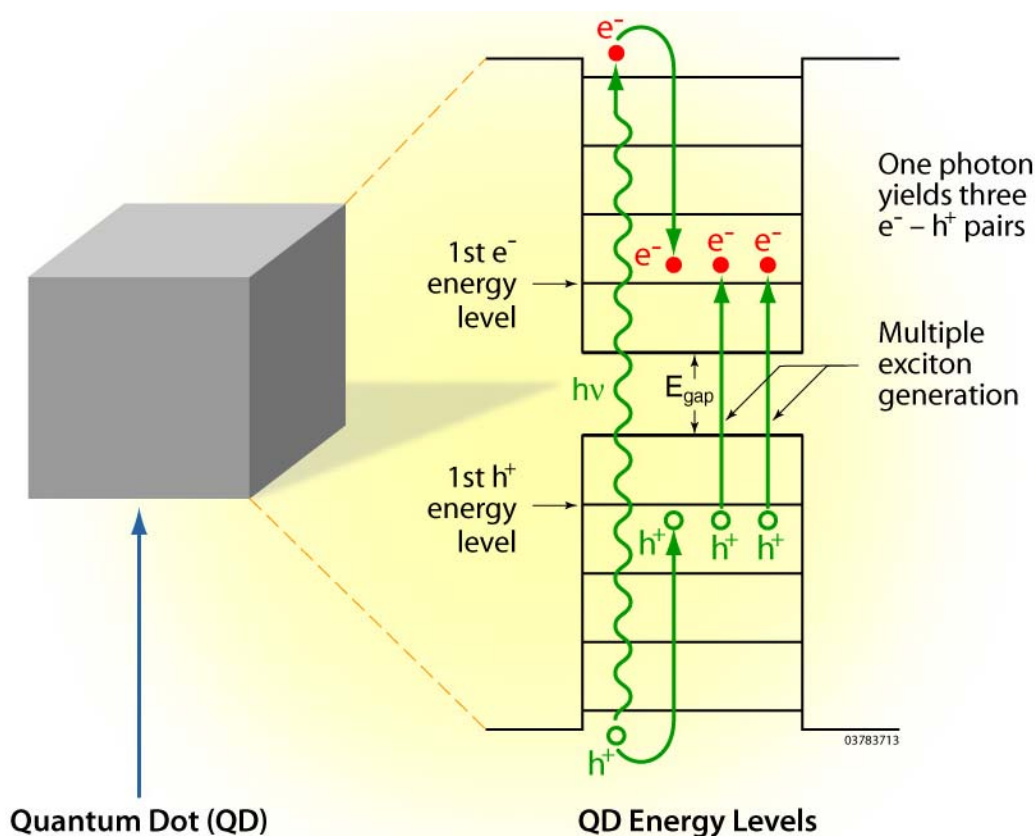
Figure 22 Multiple exciton generation in quantum dots. Because of quantum confinement in the small nanoscale semiconductor QD particle, the energy levels for electrons and holes are discrete. This slows hot exciton cooling and enhances multiple exciton formation. A single absorbed photon that has an 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)
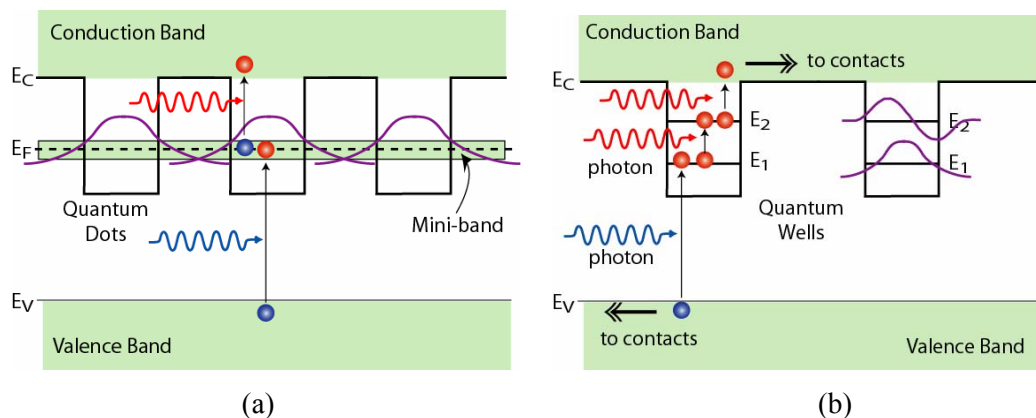
Figure 23 (a) Intermediate band solar cell and (b) quantum well solar cell

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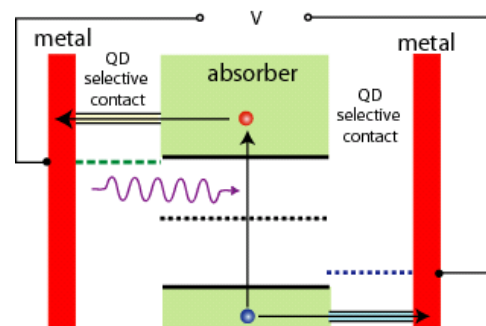
Figure 24 In hot carrier solar cells, carriers are collected before they thermalize.

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.
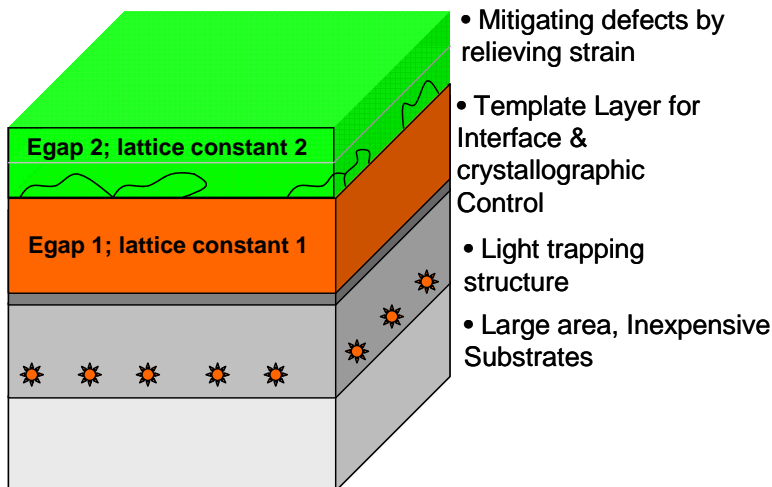

Figure 25 Integration of dissimilar materials to harness sunlight

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.
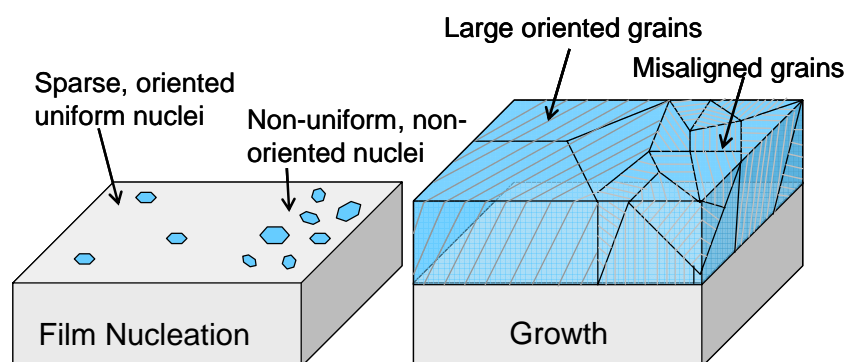
Figure 26 Controlling nucleation and growth

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.

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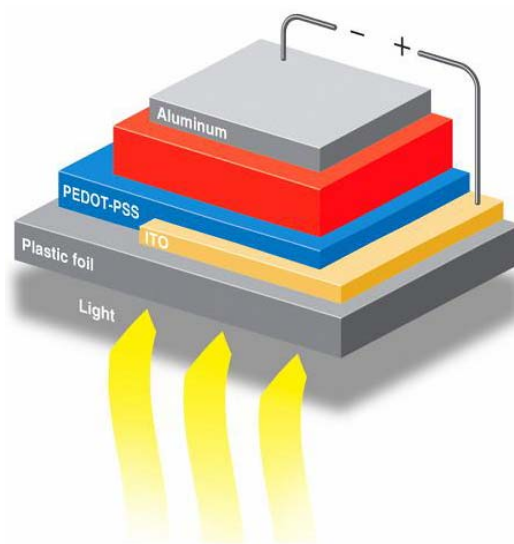# MAXIMUM ENERGY FROM SOLAR PHOTONS AT LOW COST: DESIGNED PLASTIC PHOTOVOLTAIC STRUCTURES

"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
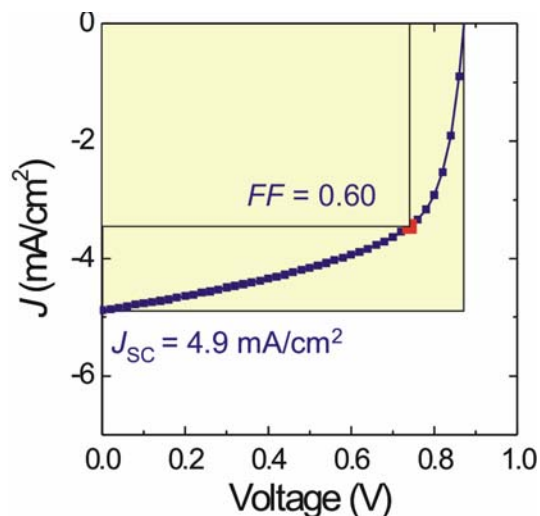
these new organic structures, and to maximize energy extraction efficiencies. The research will strive to achieve new, low-cost, scalable fabrication methods.

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

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%
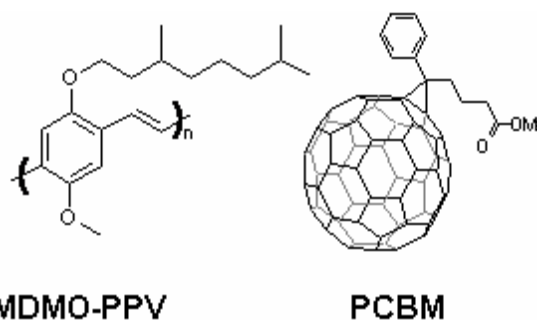
Figure 29 A typical conjugated polymer (MDMO-PPV) and a soluble derivative of C_{60} (PCBM) used in a bulk heterojunction device

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

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
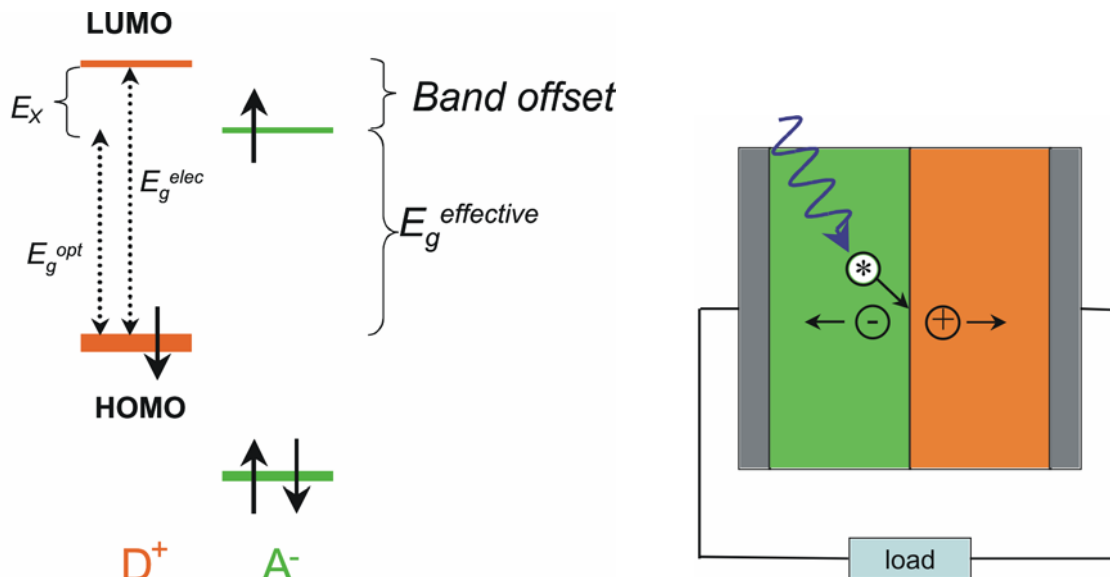
Figure 30 Schematic diagram (right) of an excitonic solar cell comprising a donor (orange) and an acceptor (green) species. An energy-level diagram (left) with excitation into the donor shows the optical and electronic bandgaps of the donor and acceptor and the band offset relative to the exciton binding 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
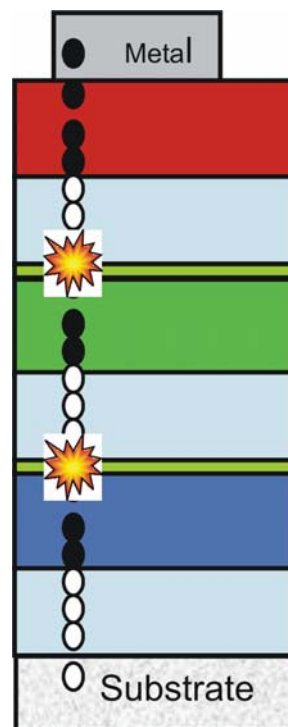
Figure 31 Schematic of a multi-layered, tandem organic solar cell with three stacked solar cells designed to absorb different solar photons that enter through the substrate. Balanced charge transport in each cell is indicated with efficient recombination at the two interconnectors.

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.

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# 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
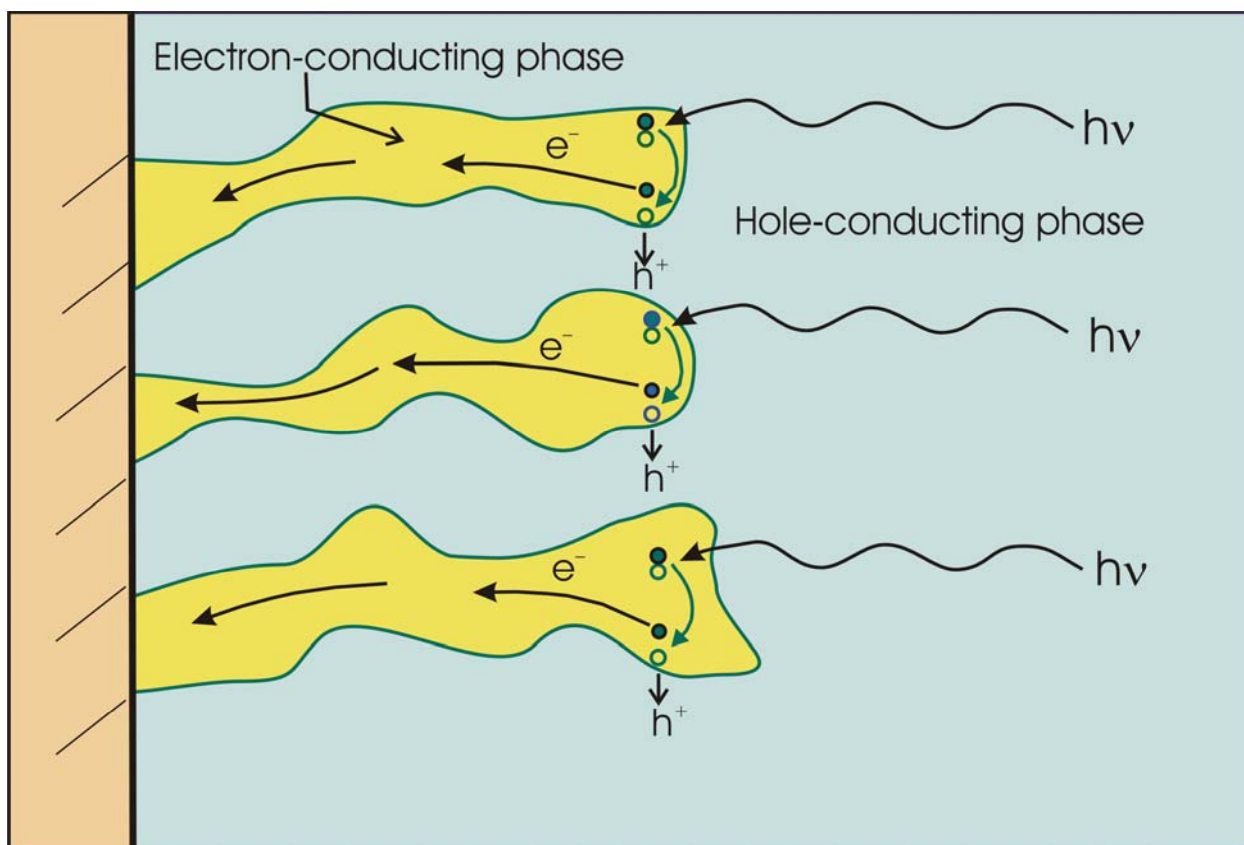
Figure 32 One important example of such a structure is provided by mesoscopic dye-sensitized solar cells (Grätzel 2000; Grätzel 2001), which generally involve use of a highly porous film of randomly ordered nanoparticles of a transparent nanocrystalline oxide, such as TiO_2, coated with an ultra-thin 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.
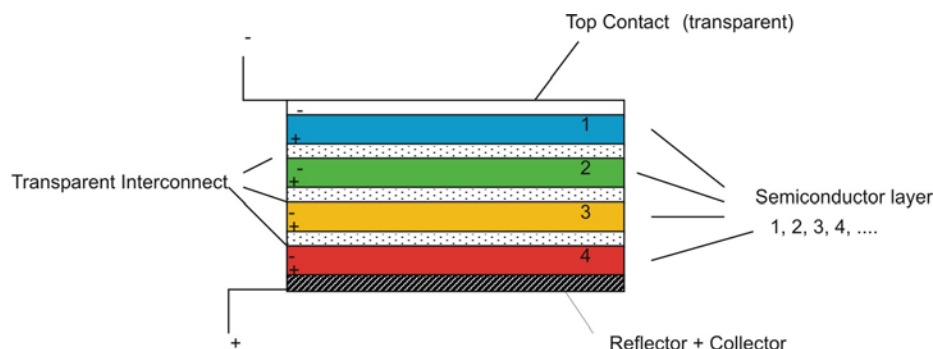
Figure 33 Quadruple junction solar cell comprising sensitized mesoscopic oxides of different color or thin-film photovoltaic cells as light-absorbing layers. The theoretical conversion efficiency of such a device is close to 50%.

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.

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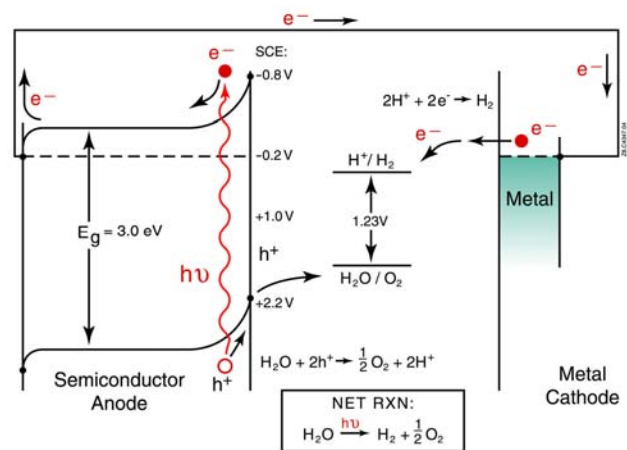
FUELS FROM WATER AND SUNLIGHT: NEW PHOTOELECTRODES FOR EFFICIENT PHOTOELECTROLYSIS

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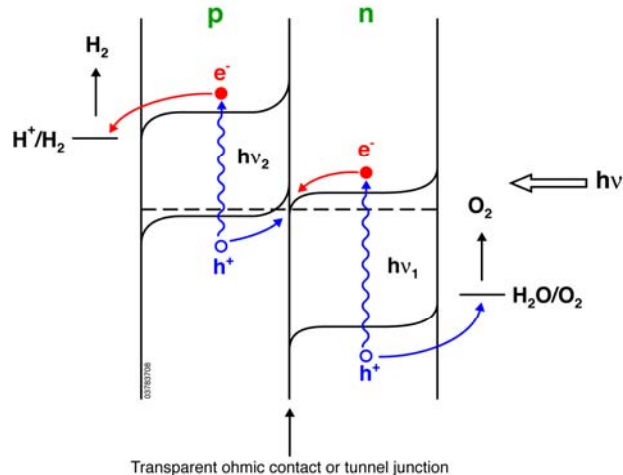
Figure 35 p-n Photoelectrolysis cell (photochemical diode). The n-type anode and p-type cathode are connected in a bi-layered monolithic structure through a contact that produces electron-hole recombination to permit charge balance. (Source: Nozik 1977)

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.

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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.
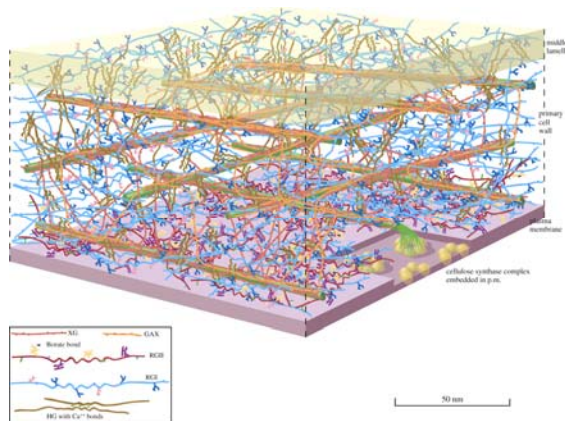
SUMMARY OF RESEARCH DIRECTION

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.
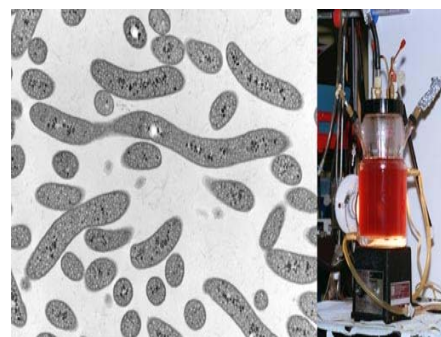
CELL WALL BIOSYNTHESIS AND BIOFUEL PRODUCTION

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
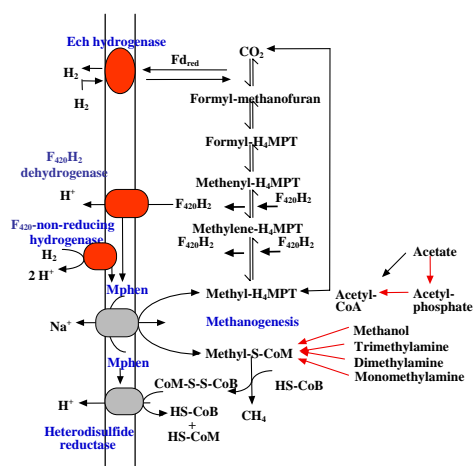
been made in identifying and characterizing the various enzymes involved in microbial digestion of lignocellulose. However, in many cases, the enzymes or enzyme complexes found in nature are not well-suited to industrial-scale processes for conversion of lignocellulose to fermentable sugars and other 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.

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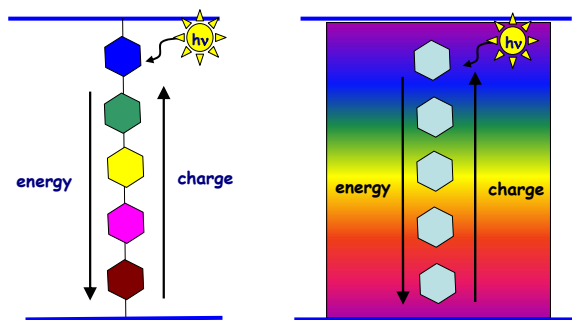
Figure 39 A smart matrix. Left: The present situation for transporting energy or charge with covalently linked, synthetically tuned chromophores. Right: Self-assembled chromophores whose properties are tailored by the smart matrix.

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.
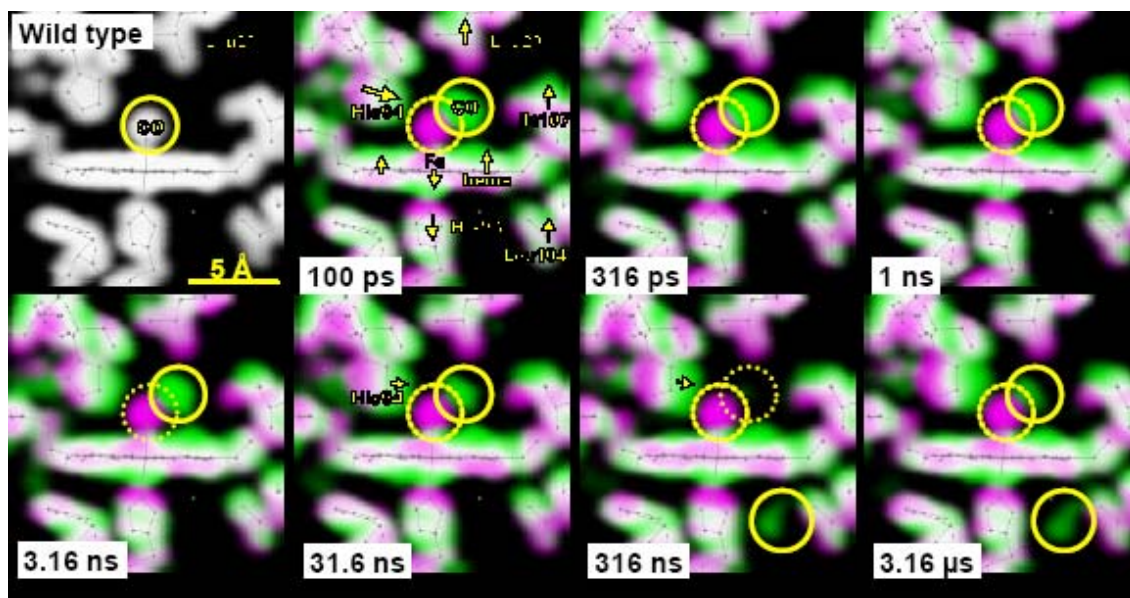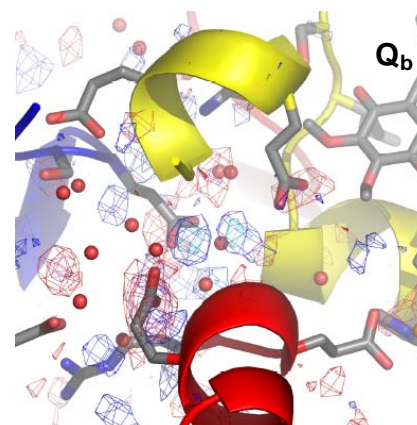
Figure 40 X-ray diffraction determined snapshots with 100-ps time-resolution of atomic motions coupled to CO photolysis in myoglobin, achieved using pump-probe X-ray crystallographic techniques (Source: Schotte et al. 2004)

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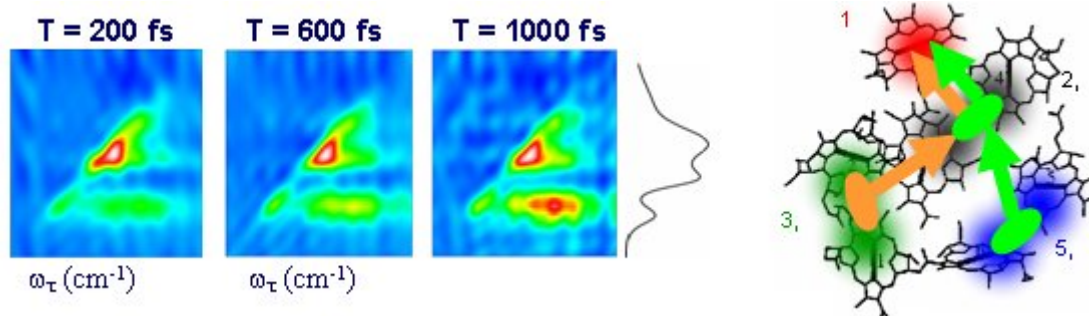
Figure 42 Dynamically resolved electronic coupling in the FMO protein using 2-D pulsed spectroscopy (Source: Brixner et al. 2005)

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.

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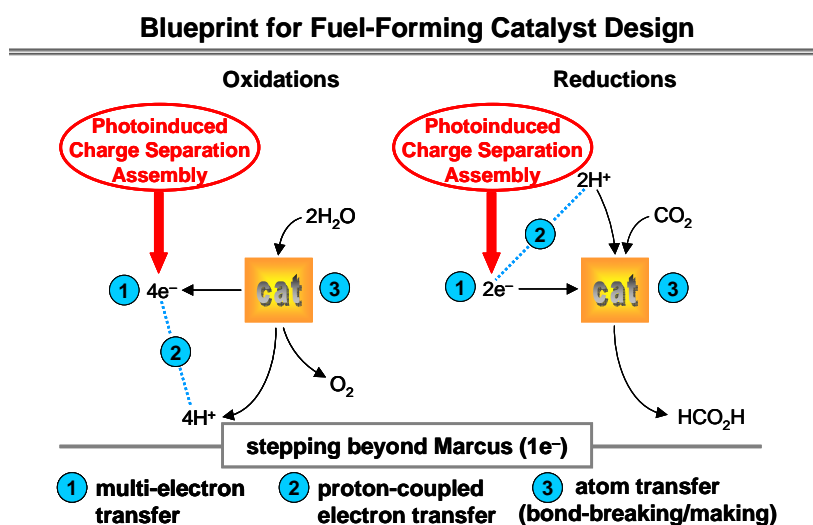
Figure 43 A blueprint for catalyst design detailed for both oxidation and reduction catalysts (Cat = catalyst)

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
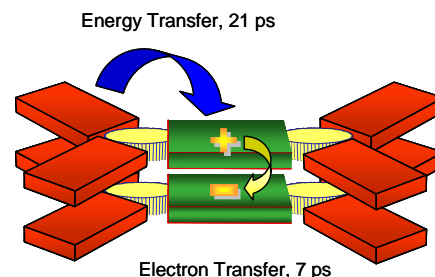
largely unknown are the fundamental concepts of how to prepare individual light-harvesting complexes, reaction centers, or catalysts that can readily engage in specific intermolecular interactions promoting their assembly into ordered supramolecular structures with the ability to function as complete 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.

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.

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)

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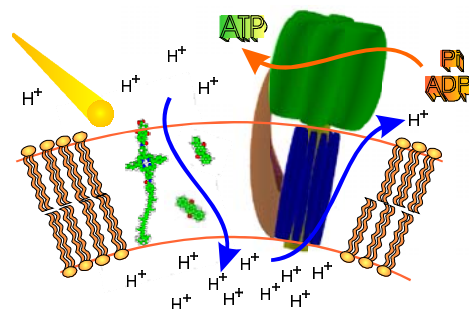
Figure 45 Hybrid light-driven proton pump using charge separation within a donor-acceptor triad and ATP synthase incorporated into a liposome (Source: Steinberg-Yfrach et al. 1998)

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.

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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
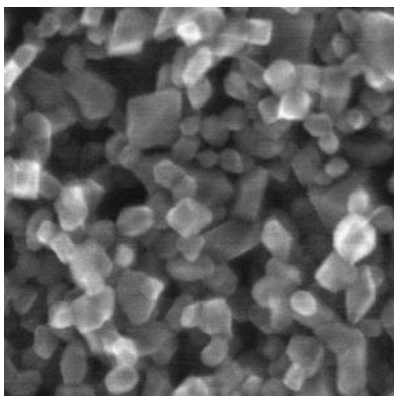
Figure 46 Defect-tolerant solar cell: dye-sensitized solar cell using defective nanoparticulate TiO$_2$ as electrodes

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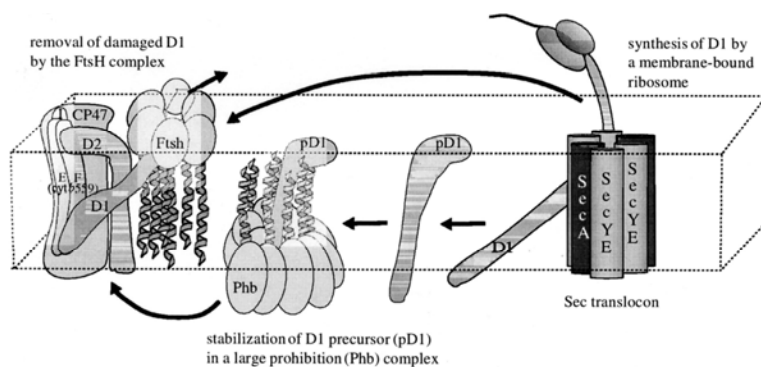
Figure 47 Repair of PSII by degrading photo-damaged D1 protein and replacing it with newly synthesized D1 protein

146

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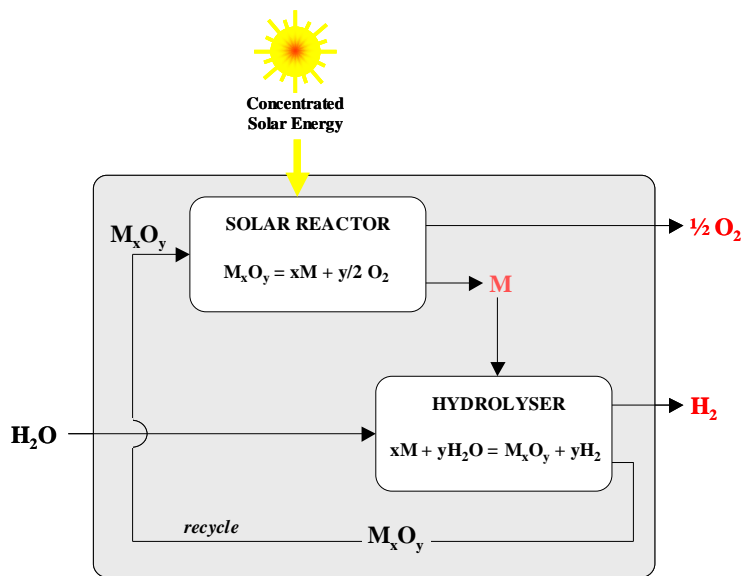
Figure 48 Solar hydrogen production by water-splitting thermochemical cycle via metal oxide redox reactions

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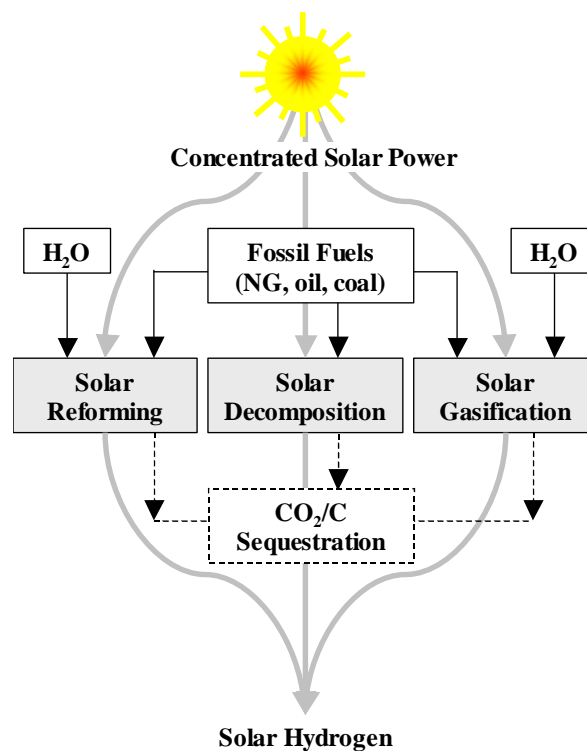
Figure 50 Scheme of three hybrid solar thermochemical routes for the production of hydrogen by thermal decarbonization of fossil fuels: solar decomposition, solar reforming, and solar gasification

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.

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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.
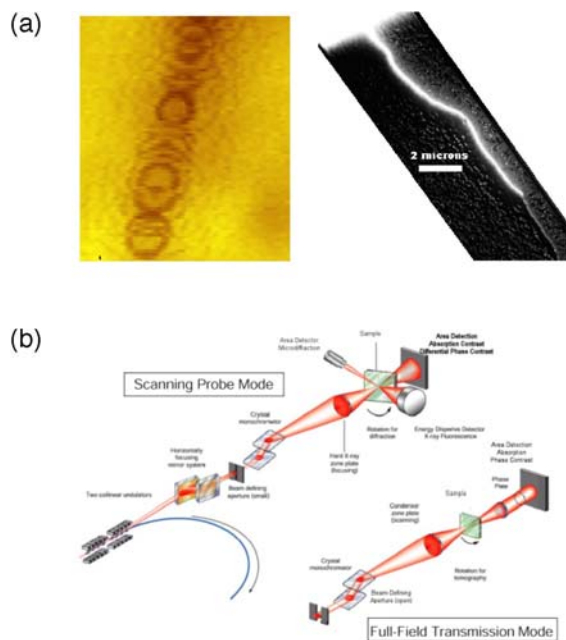
Research Needs

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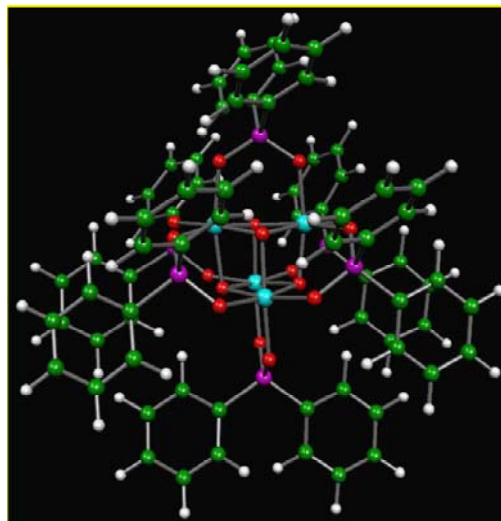
Figure 53 Density functional theory calculations give the optimized geometry of a $(Ph_2PO_2)_6Mn_4O_4$ cubane complex (a quasi-cubane Mn cluster) that is relevant to photosynthesis.

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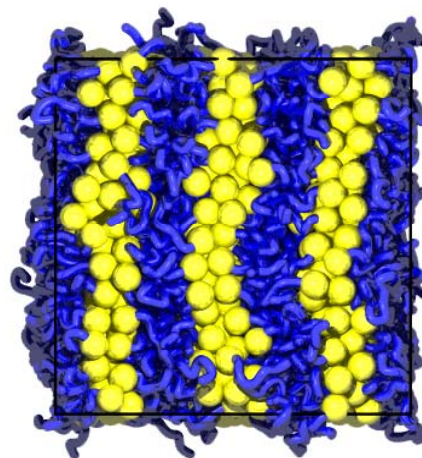
will require significant new progress even at the level of basic theory, let alone computational algorithms and their numerical implementation. For instance, successful modeling will require effective schemes for non-adiabatic quantum molecular dynamics and schemes for quantum transport in the presence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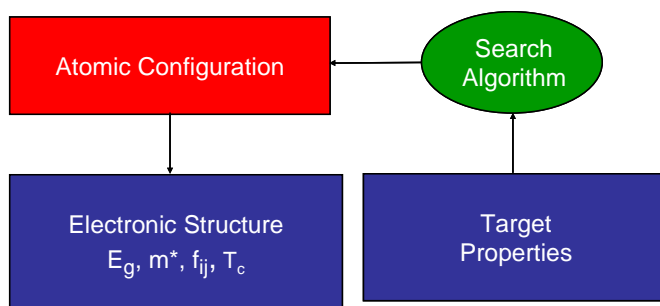
RESEARCH DIRECTIONS

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

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.

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.

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
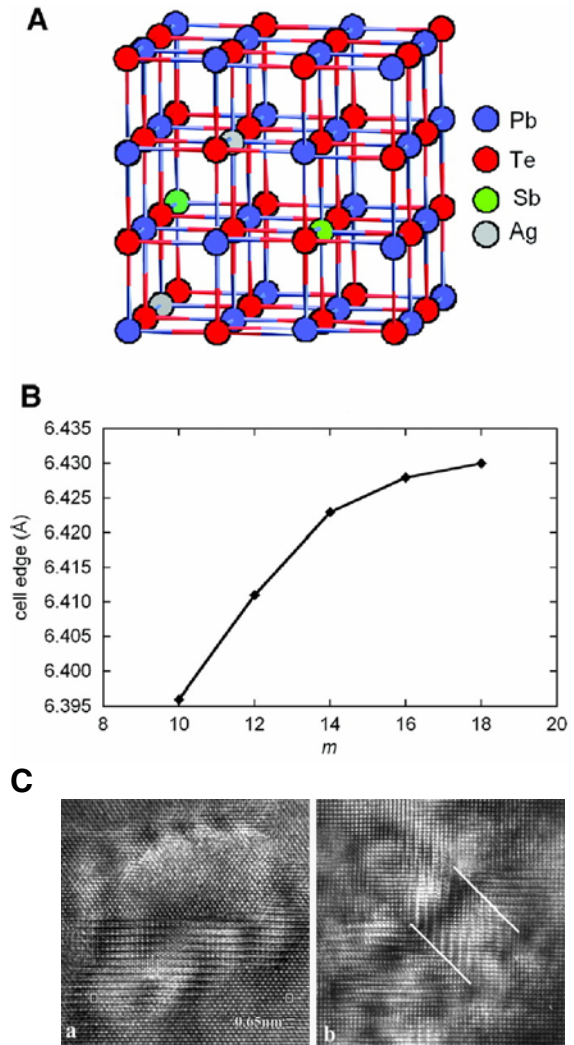
Figure 56 The difficulty of searching experimentally for the optimal high-ZT material is illustrated in this figure. AgPbmMTe2+m (where M is either Sb or Bi and m varies from 10 to 18) is a candidate for a high ZT material. What is the optimal composition? Fig. 56A shows the average ideal crystal structure; 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.
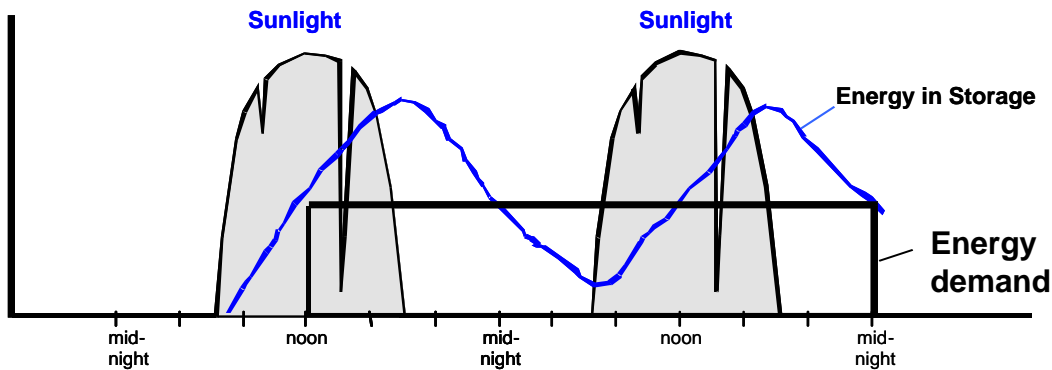
Figure 57 Example of the periodic variation of incident sunlight and thermal energy in the storage, relative to energy demand

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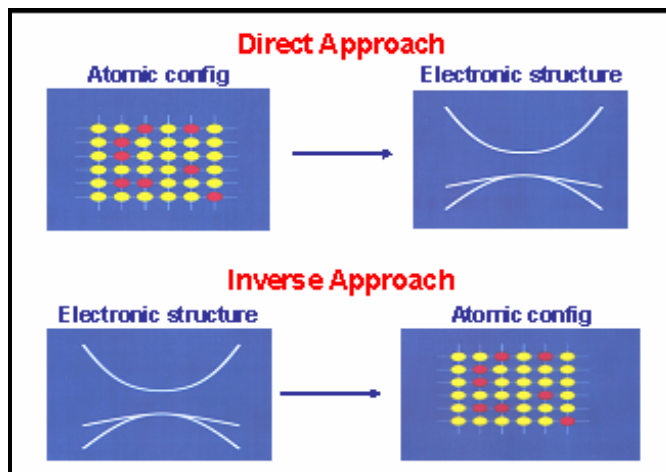
Figure 58 Inverse electronic structure calculations. In the direct approach, the modeler starts with a given atomic configuration and calculates the electronic structure. In the inverse approach, the modeler is told the electronic structure and must search to find an atomic configuration that will produce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

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.
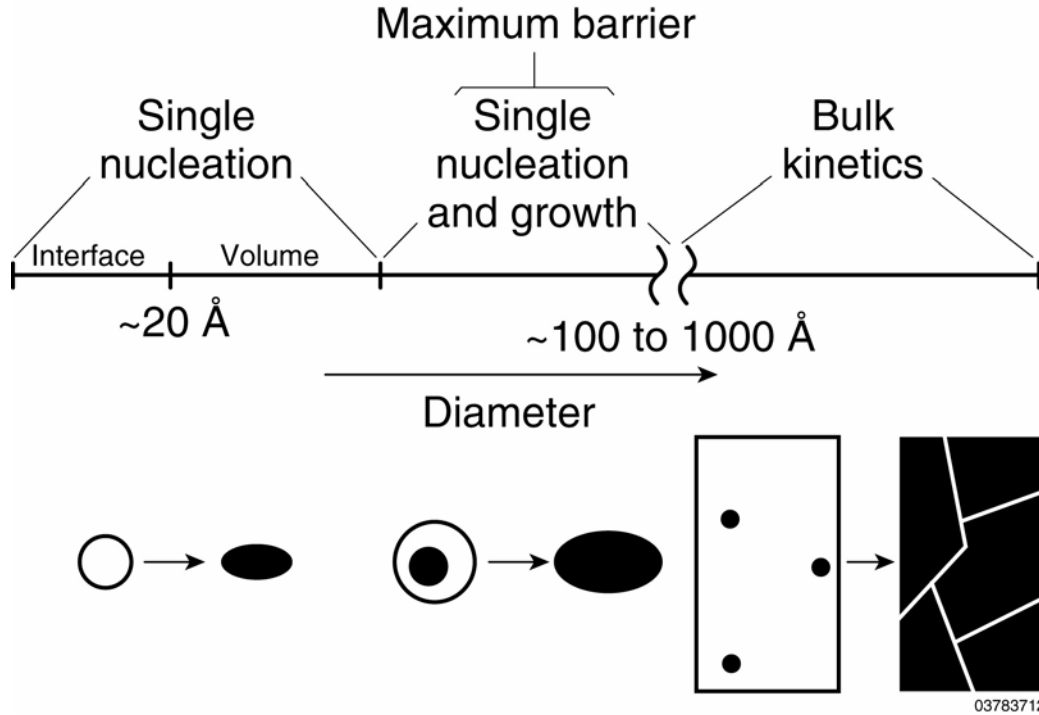
Figure 59 Illustration of various size regimes of the kinetics of solid-solid phase transitions. Defects, which act as nucleation sites, are indicated by asterisks in the cartoon of the bulk solid.

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.

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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.
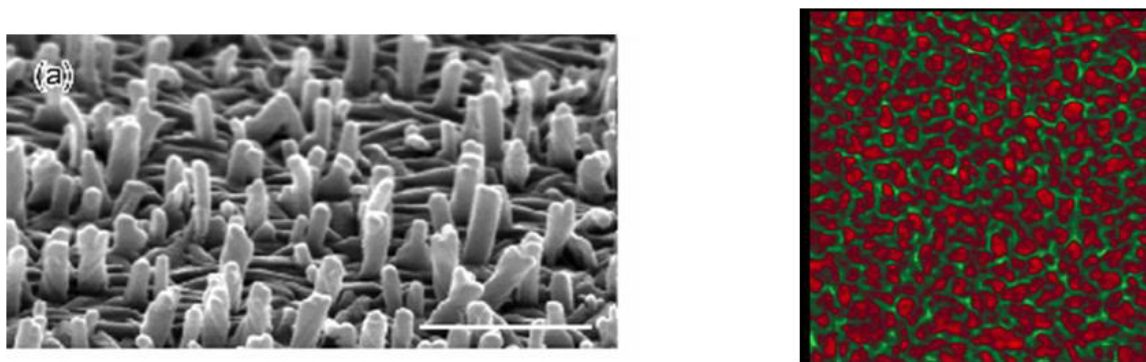

Figure 60 Bulk heterojunction structures. (a) Left: Controlled growth by vapor deposition of a small molecule material into pillars which can give rise bulk heterojunction solar cell material. (b) Right: Bulk heterojunction formed by nanophase segregation of organic PV materials.

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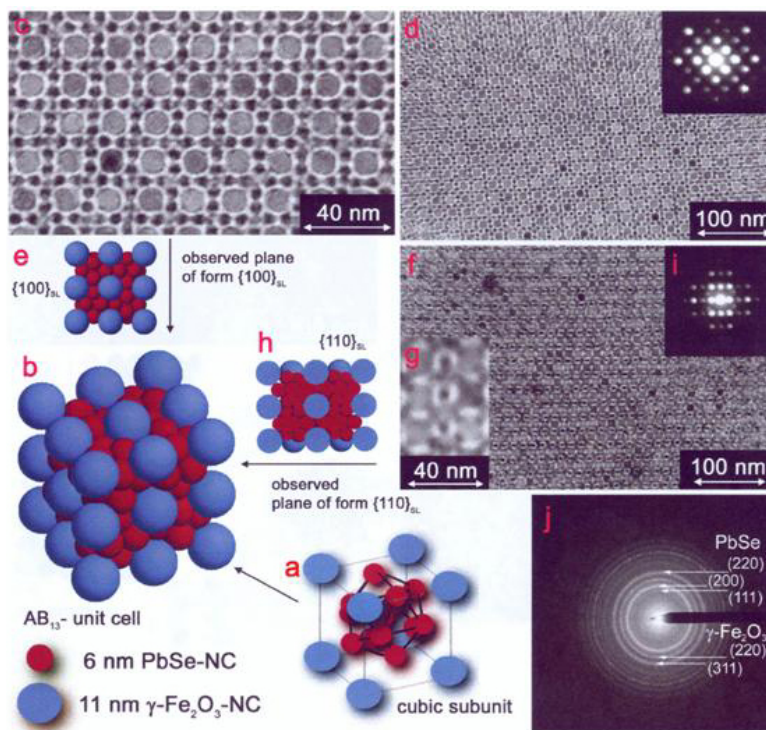
Figure 61 Superlattice formation via self-assembly of inorganic nanocrystals (Source: Redl et al. 2003)

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.
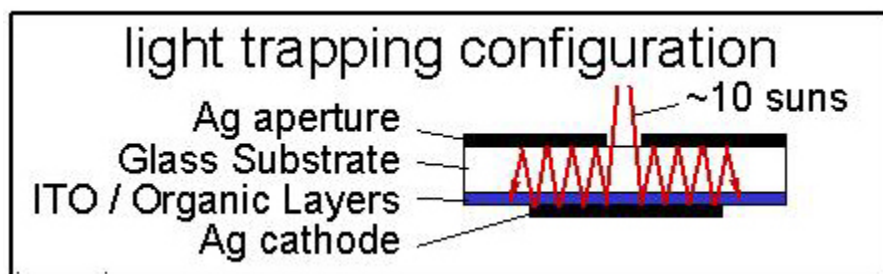

Figure 62 Light-trapping by concentrator/waveguide structure increases light absorption efficiency.

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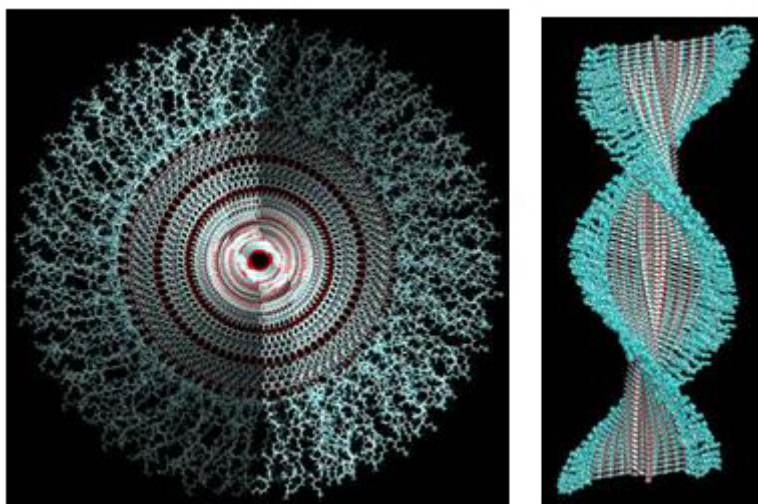
Figure 63 Self-assembling organic nanoribbons (Source: S. Stupp, Northwestern University, unpublished)

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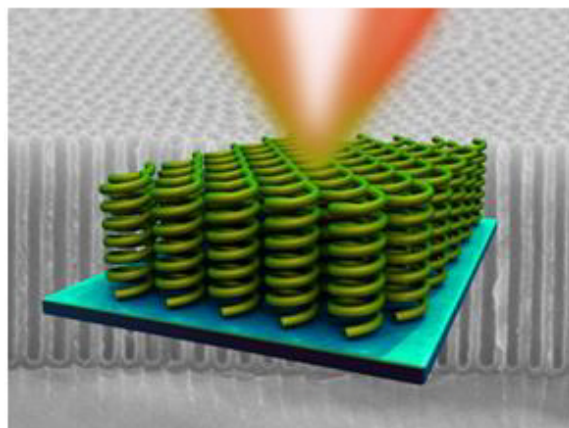
TMS will be used to discover the design rules for reverse-engineering building blocks capable of self-assembling into target structures.

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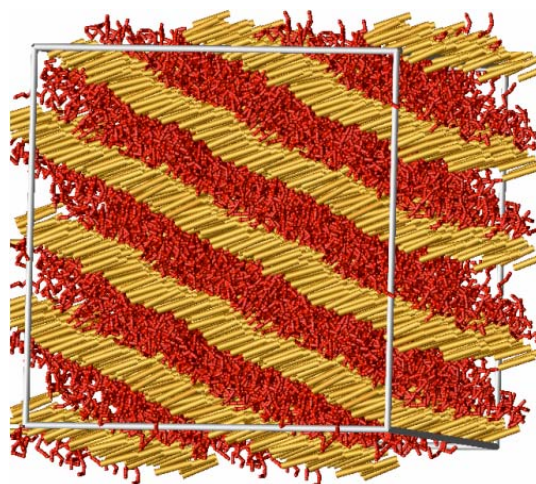
Figure 65 Theoretical simulation for nanorod self-organization into smectic phase (Source: S. Glotzer, University of Michigan, unpublished)

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.

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CONCLUSION

CONCLUSION

Global demand for energy will more than double by mid-century and more than triple by the century's end. Meeting this demand is society's foremost challenge for achieving vibrant technological progress, economic growth, and political stability over the next 50 years. Incremental advances in existing energy technologies will not bridge the gap between today's production and tomorrow's needs. Additional energy sources must be found over the next half-century with the capacity to duplicate today's energy output.

The Sun is the champion of energy sources. It delivers more energy to Earth in an hour than we use in a year from fossil, nuclear, and all renewable sources combined. Its energy supply is inexhaustible in human terms, and its use is harmless to our environment and climate. Despite the Sun's immense capacity, we derive less than 0.1% of our primary energy from sunlight.

The enormous untapped potential of the Sun is a singular opportunity to meet our future energy needs. The Basic Energy Sciences Workshop on Solar Energy Utilization examined three routes for converting sunlight to useful energy through electricity, fuels, and heat. These energy conversion products couple naturally into our existing energy networks. The Workshop identified 13 high-priority research directions with the potential to eliminate the huge gap separating our present tiny use of the solar resource from its immense capacity. Bridging this gap requires revolutionary breakthroughs that come only from basic research. We must understand the fundamental principles of solar energy conversion and develop new materials that exploit them.

There is considerable common ground underlying the three conversion routes of sunlight to electricity, fuel, and heat. Each follows the same functional sequence of capture, conversion, and storage of solar energy, and they exploit many of the same electronic and molecular mechanisms to accomplish these tasks. A major challenge is tapping the full spectrum of colors in solar radiation. The absorbing materials in the current generation of photocells and, artificial photosynthetic machines typically capture only a fraction of the wavelengths in sunlight. Designing composite materials that effectively absorb all the colors in the solar spectrum for conversion to electricity, fuel, and heat would be a crosscutting breakthrough.

Captured solar energy must be transported as excited electrons and holes from the absorber to chemical reaction sites for making fuel or to external circuits as electricity. Nature transmits excited electrons and holes without energy loss through sophisticated assemblies of proteins whose function we are just beginning to understand with genome sequencing and structural biology. These "smart materials" react to the local molecular environment to protect their precious cargoes and hand them off to neighboring functional units when the molecular stage is properly set. Understanding and adapting nature's methods of electron and hole manipulation would create revolutionary new approaches to transferring captured solar energy within materials.

Materials discoveries often launch revolutionary new development routes. Photovoltaic conversion is now looking at a host of new materials to replace silicon, including inexpensive organic semiconductors ("plastic photocells"), thin polycrystalline films, organic dye injectors,

and quantum dots. Quantum dots are especially exciting for their tunable absorption wavelength, their quantum conversion efficiency above 100% through multiple-exciton generation, and their easy fabrication through self-assembly. The diversity of new materials in accessible nanoscale architectures promises to spawn breakthroughs in photovoltaic concepts and performance that could break the 50% efficiency level.

Solar thermal conversion is one of the most promising directions of solar energy research. Almost all our existing energy networks rely on heat and heat engines as essential links, from industrial processing of chemicals to electricity production to space heating itself. Most of the required heat is produced by combustion of fossil fuels, but it could be supplied as effectively by solar thermal conversion. Solar concentrators produce temperatures up to 3,000°C, far hotter than conventional furnaces and capable of driving reactions like splitting water or decomposing metal oxides that produce chemical fuel without expensive catalysts. Lower-temperature heat can be used to drive steam engines that produce electricity from sunlight with 30% efficiency, higher than the present generation of commercial photocells. Reduced cost, higher efficiency and longer lifetime for solar space-heating systems would create enormous energy impact. Promising breakthrough directions for solar thermal research are materials that can withstand the high temperatures and corrosive chemical environments in solar furnaces, and materials for high-capacity, slow-release thermal storage. The ability to accumulate heat during the day, possibly storing it in an embedded phase transition, and release it in a controlled manner at night would enable solar thermal applications to operate 24 hours per day.

Research in solar energy conversion sits squarely at the intersection of physics, chemistry, biology and nanoscience. Photosynthesis is the most successful solar energy converter on Earth, converting 90 TW of solar energy to sugars and carbohydrates. Through advances in structural biology, genome sequencing, and proteomics, we are learning the molecular pathways of photosynthesis, and beginning to reproduce some of its simpler functions in artificial self-assembled structures in the laboratory. The insights generated by these fascinating studies will enable us to produce faster-growing energy crops; adapt the cheap, efficient catalysts of enzymes to synthetic solar conversion schemes; and create artificial molecular machines that turn sunlight, water, and CO_2 into chemical fuel. Photovoltaic systems are turning to organic semiconductors and metal oxide-organic dye composites for cheaper high performance materials. Organic molecules display a host of novel photo-excitation and electron transfer phenomena that open promising and still-uncharted new horizons for photovoltaic conversion. Biology provides energy conversion paradigms that are qualitatively different from those of hard materials. The biological concepts of self-repair and defect-tolerant networks give plants lifetimes of 30 years or more. Their application to artificial photovoltaic and solar thermal conversion systems promises to dramatically extend their useful lives.

The physical, chemical, and biological pathways of solar energy research meet in nanoscience. Top-down and bottom-up fabrication of complex nanoscale architectures enables assembling and interconnecting functional molecular units for solar energy capture, conversion, and storage with precision and reliability never before attainable. Scanning probe microscopies on the benchtop, electron microscopy with atomic resolution, and in situ experiments at high-intensity X-ray and neutron sources can now reveal the structure and dynamics of solar conversion at the molecular level. Sophisticated quantum chemistry simulations using density functional theory can now predict the electronic and structural behavior of multithousand atom clusters like those that

mediate solar conversion. These emerging tools of nanoscale fabrication, characterization, and simulation bring fundamental understanding and control of the molecular mechanisms of solar energy conversion within reach. The cross-fertilization of nanoscale biology, chemistry, and physics is a new feature that creates fascinating interdisciplinary routes to solar conversion. The strong need for doubling our energy output in the next half-century, the singular capacity of the sun as a source of clean, abundant energy, and rapid advances in the physics, chemistry and biology of solar conversion at the nanoscale are compelling motivation for a coordinated basic research program on solar energy utilization.

APPENDIX 1: TECHNOLOGY ASSESSMENTS

SOLAR ELECTRICITY

BACKGROUND OF PHOTOVOLTAICS

A diagram of a *p-n* junction photovoltaic (PV) solar cell is shown in Figure 66. The solar spectrum at air mass 1.5 (AM1.5) (solar intensity at Earth's surface with sun at 42º elevation from the horizon) is shown in Figure 67a; the maximum conversion efficiency of single-band-gap solar cells as a function of the semiconductor band gap, assuming full electron-phonon relaxation, is shown in Figure 67b.
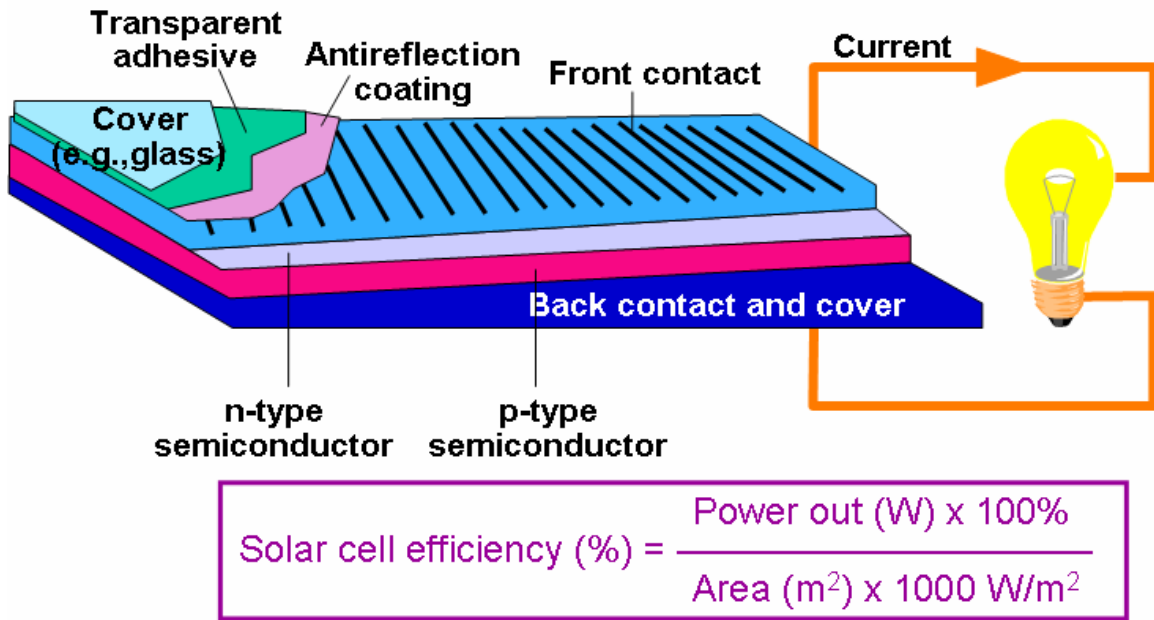
Figure 66 A *p-n* junction PV solar cell
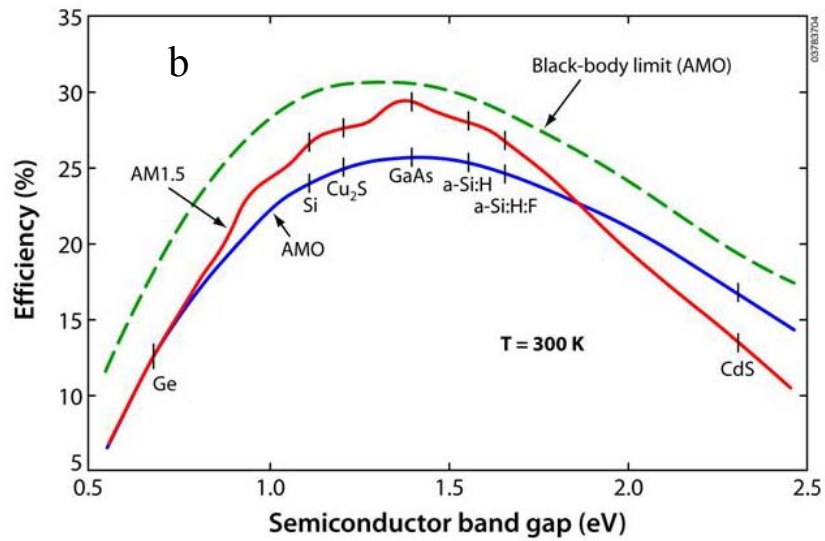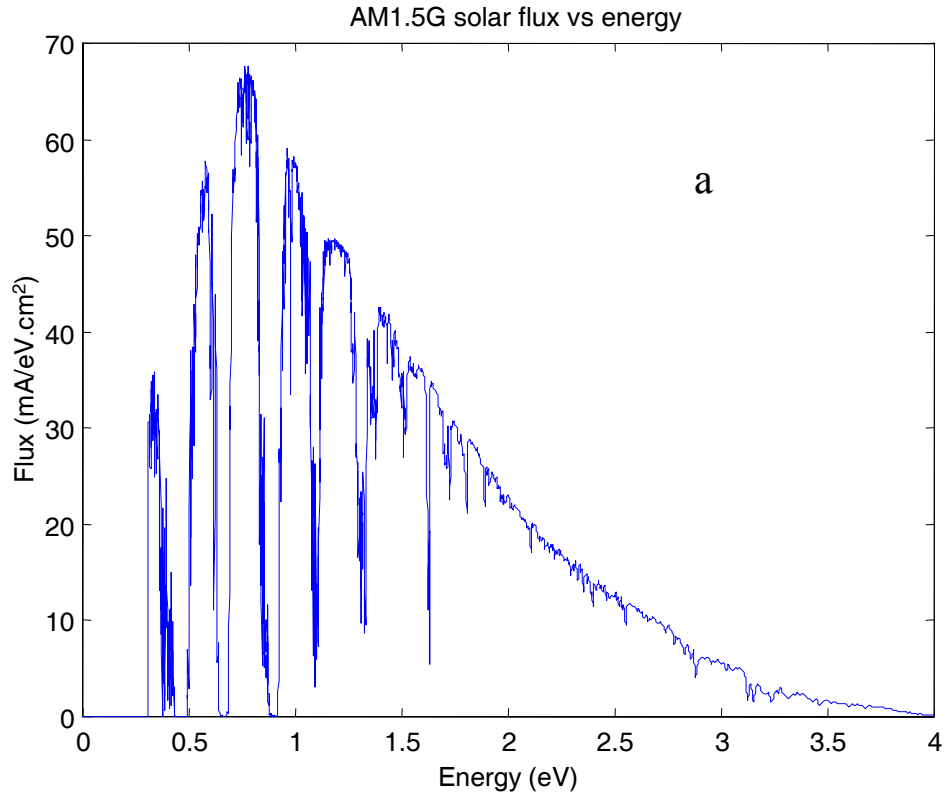
Figure 67 (a) Solar spectrum at AM1.5, where the range of human vision runs from 3.1 eV (violet) to 1.9 eV (red); (b) maximum conversion efficiency of a single junction cell vs. band gap

Cost of PV Electricity

The cost of PV electricity is determined from solar cell conversion efficiency together with areal cost of the module. The relationships are simple:

$$C = \$/\text{peak watt} = (\text{module areal cost/Eff}) + (\text{BOS areal cost/Eff}) + 0.10, \qquad (1)$$

where

C = cost per watt of incident solar irradiance at peak solar intensity, $\$/W_p$

Eff = converted solar power (fractional conversion efficiency $\times$ 1,000 W/m^2), W_p/m^2

Module areal cost = cost of modules only per unit area, $\$/m^2$

BOS areal cost = balance of systems (support structure, installation, wiring, land, etc.) cost per unit area, $\$/m^2$

$0.10 = cost of power conditioning, AC-DC inverter, $\$/W_p$

Then, taking into account the cost of capital funds, interest rates, depreciation, system lifetime, and the available annual solar irradiance integrated over the year (i.e., considering the diurnal cycle and cloud cover, which reduce the peak power by a factor of about 5), cost per peak watt $\$/W_p$ can be converted to $/kWh from the simple relationship:

$$1\$/W_p \approx \$0.05/\text{kWh} \qquad (2)$$

Currently, silicon PV module costs are about $350/m^2 and BOS costs are about $250/m^2, so that with present silicon module conversion efficiencies of 10%, C ~ $6/W_p$, and the electrical energy costs are about $0.30/kWh.

Solar electricity is currently more than a $7 billion per year business, growing at more than 40% per year.

PV TECHNOLOGY OPTIONS — FLAT PLATE OR CONCENTRATORS

Photovoltaic technologies can be divided into two main approaches: flat plates and concentrators. Flat-plate technologies include crystalline silicon (from both ingot and ribbon- or sheet-growth techniques) and thin films of various semiconductor materials, usually deposited on low-cost substrate, such as glass, plastic, or stainless steel, using some type of vapor deposition, electrodeposition, or wet chemical process. Thin-film cells typically require one-tenth to one-hundredth of the expensive semiconductor material required by crystalline silicon. Even thinner layers are involved in some of the future generation technologies, such as organic polymers and nanomaterials. In the case of concentrators, a system of lenses or reflectors made from less expensive materials is used to focus sunlight on smaller, somewhat more expensive, but highly efficient solar cells. Table 1 provides a breakdown of PV module production in 2003 by technology.

Table 1 Worldwide PV Module Production in 2003 by Technology Type

Technology Type	MW	%
Flat plates – single-crystal silicon	230.5	31.0
Cast poly/multicrystalline silicon	443.8	59.6
Ribbon silicon	22.8	3.1
Thin-film amorphous silicon	39.3	5.3
Thin-film cadmium telluride	3	0.4
Thin-film CIGS	4	0.5
Concentrators – silicon	0.7	0.1
TOTALS	**744.1**	**100**

Source: *PV News*

Flat-plate Systems

Flat-plate Crystalline Silicon. Of the PV modules produced today, nearly 94% are based on crystalline silicon wafer technologies. Of this total, about 30% are based on conventional, single-crystal silicon grown by the Czochralski ingot process, 60% are based on polycrystalline (also referred to as multicrystalline) ingots cast in a crucible, and 3% are from silicon ribbons/sheet produced by various processes.

Ingot-based Technologies. The silicon solar cells with the highest efficiency to date (24.7% in Figure 66) have been made with single-crystal, float-zone silicon, but the commercial use of float-zone silicon for PV has started only recently. Using back-contact solar cell design, 21.5% efficiency has been achieved with long lifetime (>1 ms), n-type float-zone silicon wafers (Mulligan et al. 2004).

Single-crystal silicon grown by the Czochralski technique still constitutes a sizable portion of the PV market (Table 1). Several cell designs have achieved efficiencies of >21% (Tanaka et al. 2003) and >18% (Bruton et al. 2003). Efforts to improve Czochralski growth for PV typically focus on reducing consumable materials and energy costs — melt replenishment, crucible development (lower cost and longer lifetime), furnace hot-zone designs, growth ambient control, increase in ingot diameter and length, and extensive studies of the effects of defects and impurities.

By far the fastest growing segment of the PV industry (Table 1) is that based on casting large, multicrystalline ingots in some crucible that is usually consumed in the process. The grain sizes are typically in the millimeter to centimeter range in width and columnar (several centimeters in length) along the solidification direction. Manufacturers routinely fabricate large multicrystalline silicon solar cells with efficiencies in the 13–15% range; small-area research cells are 20% efficient.

Non-ingot-based Technologies. Silicon ribbon or sheet technologies avoid the costs and material losses associated with slicing ingots. The current commercial approaches in the field are the edge-defined, film-fed growth (EFG) of silicon ribbons and the string ribbon process.

In the current EFG process, an octagonal cylinder, with 12.5-cm-wide flat faces, is pulled directly from the melt by using a graphite die to define its shape. The octagons are cut into wafers with an automated laser system. The ribbon thickness is typically 250–300 μm, and the growth rate is typically 2–3 cm/min.

The string ribbon process has evolved rapidly from conception to commercial production. In this simple, very stable process, two high-temperature string materials are brought up through small holes in the bottom of a shallow graphite crucible containing the silicon melt. The strings stabilize the ribbon edges and result in continuous growth (with melt replenishment using granular silicon feedstock). The strings are nonconductive and are left in the ribbon through cell/module processing. The ribbon thicknesses and growth rates are similar to those in EFG; the ribbon width is currently 8 cm. The material quality of EFG and string ribbons is similar to the multicrystalline wafers, and 14%-efficient cells are routinely fabricated.

Other Approaches under Development. Full-scale production of silicon modules based on micron-sized silicon spheres was recently announced. In this process, sub-millimeter-size silicon spheres are bonded between two thin aluminum sheets, processed into solar cells, and packaged into flexible, lightweight modules. Another approach uses a micromachining technique to form deep narrow grooves perpendicular to the surface of a 1- to 2-mm-thick single-crystal silicon wafer. This results in large numbers of thin (50 μm), long (100 mm), narrow (nearly the original wafer thickness) silicon strips that are processed into solar cells just prior to separation from the wafer. In a final technique, a carbon foil is pulled through a silicon melt, resulting in the growth of two thin silicon layers on either side of the foil. After the edges are scribed and the sheet is cut into wafers, the carbon foil is burned off resulting in two silicon wafers (150 μm thick) for processing into solar cells.

Flat-plate Thin Films. Thin-film technologies have the potential for substantial cost advantages over wafer-based crystalline silicon because of factors such as lower material use (due to direct band gaps), fewer processing steps, and simpler manufacturing technology for large-area modules. Many of the processes are high throughput and continuous (e.g., roll-to-roll); they usually do not involve high temperatures, and, in some cases, do not require high-vacuum deposition equipment. The process of module fabrication, involving the interconnection of individual solar cells, is usually carried out as part of the film-deposition processes. The major systems are amorphous silicon, cadmium telluride, and copper indium diselenide (CIS) and related alloys. Figure 3 illustrates the significant progress in laboratory cell efficiencies in these technologies. Future directions include multijunction thin films aimed at significantly higher conversion efficiencies, better transparent conducting oxide electrodes, and thin polycrystalline silicon films.

Amorphous Silicon. From its discovery in the early 1970s, hydrogenated amorphous silicon (a-Si:H) has stimulated a large worldwide effort to develop various semiconductor device applications. The main advantage of a-Si:H for PV is the low materials and manufacturing costs. The films can be deposited on ordinary window glass, as well as on flexible substrates (stainless steel or polyimide), to make PV products such as flexible roofing shingles, semitransparent modules for windows or skylights, and portable power modules. The basic cell structure is a *p-i-n* structure, with an undoped (intrinsic) a-Si:H layer between two very thin doped layers. This structure produces an electric field throughout the cell to separate photogenerated electrons and holes and produce electricity. The main disadvantage of a-Si:H is the modest efficiency that has been achieved to date. Stable, small-area cell efficiencies reach 13%, but the best module efficiency is 10.2% (for 1,000-cm^2 area). Most a-Si:H power modules sold today have stable efficiencies of between 6% and 8%. The higher-efficiency designs use dual- or triple-junction cell structures to capture more of the available sunlight (the band gap of a-Si:H ranges from 1.6 to 1.8 eV, depending primarily on hydrogen content). Bottom cells can be either lower-band-gap a-Si:H, a-SiGe:H, or microcrystalline silicon.

The high absorption coefficient of a-Si:H stems from its lack of crystalline order. However, this same disorder limits cell efficiencies and results in a self-limiting degradation known as the Staebler-Wronski effect, or "light-induced instability." No fundamental solution to this problem has yet been found, so solar cells are made with thin undoped layers to minimize this degradation in efficiency (about 15–25% decrease from the initial efficiency). Commercial products are stable after about one month of exposure to sunlight and are always rated at their ultimate ("stable") efficiencies.

Films of a-Si:H are made by chemical vapor deposition from SiH_4 onto a 200–300°C substrate using a radio-frequency plasma (13.56 MHz) or dc plasma. Deposition rates are typically 0.1-0.3 nm/s, meaning that a 0.6-μm-thick solar cell is deposited in less than one hour. Both batch deposition (typically for glass substrates) and roll-to-roll deposition (typically for flexible substrates) are used in production. The largest thin-film manufacturing facility today produces 30 MW/yr of a-Si:H.

Cadmium Telluride. One of the most promising approaches for the fabrication of low-cost, high-efficiency solar cells is cadmium telluride (CdTe). This material has nearly the ideal band gap for a single-junction device, and efficient solar cells have been made by a variety of potentially scalable and low-cost processes; these include close-spaced sublimation (CSS), high-rate physical vapor deposition, spraying or screen printing, solution growth, and electrodeposition. The record cell (Figure 66) is a 16.5%-efficient device, whereas the best commercial-size module is 11% efficient (typical commercial products are in the 7–9% range).

Although concerns are often raised about the environmental, health, and safety aspects associated with cadmium and tellurium, advocates of this technology believe these are mainly issues of "perception." Extensive studies have been performed concerning the manufacturing, deployment, and even decommissioning of CdTe modules. The results indicate that all safety issues can be handled at a very modest cost, including the recycling of cadmium and tellurium from old modules.

Copper Indium Diselenide. From virtual obscurity as a semiconductor material, CIS solar cells have seen remarkable progress in efficiencies (see Figure 3) with 19.3% efficiency achieved recently in CIGS (with gallium added), nearly rivaling the best polycrystalline silicon laboratory devices. Commercial-size modules with >13% efficiency have been fabricated, and early commercial products are 9–11% efficient. The layer sequence for the device structure is substrate/Mo/CIGS/CdS/ZnO. High-efficiency devices (18.6%) have also been fabricated by replacing the CdS with ZnS ("cadmium-free" devices).

The many elements in CIGS solar cells can form a great variety of compounds during film growth and cell processing, making the CIGS system very complicated. On the other hand, it is also very tolerant of defects and impurities because the chemistry, as well as the structure, can adjust in many possible ways. The most striking feature of CIGS is the tolerance of the electrical properties to deposition approaches (and hence manufacturing processes).

The substrate may be either glass or a flexible material (e.g., stainless steel or polyimide) in a roll-to-roll arrangement. Flexible, lightweight CIGS products are being sold for consumer and some military applications. The other process involves sputtering of the metals with prescribed conditions, followed by a selenization (and occasionally sulfurization) step at high temperature ($\sim$500°C, $\sim$1 hr) in a H_2Se (and H_2S) atmosphere. Several megawatts of PV products are being fabricated by this process.

Materials Supply for Present PV Systems. The issue of available future supplies of various elements used in present PV cells is summarized in Table 2.

Polycrystalline Thin-film Multijunctions. The successes to date with CdTe and CIGS recently generated efforts to develop possible routes, combinations of materials, and device structures toward demonstrating a multijunction polycrystalline thin-film solar cell with an efficiency >25% (and, ultimately, module efficiencies >20%). The materials selected for the initial studies are based on CIGS and CdTe and related alloys, but other materials are also being investigated (Symko-Davies 2004).

Thin Crystalline Silicon. An emerging thin-film technology area is thin-film crystalline silicon deposited on low-cost substrates. This possibility could combine the inherent advantages of silicon (abundance and device stability) with that of thin films (low materials use and cell interconnection during film deposition). The efforts in this area fall into two general categories. The first is to develop microcrystalline silicon bottom cells for dual- or triple-junction a-Si:H devices. The second area involves thin crystalline silicon films (thickness typically from <10 μm to a few tens of microns) deposited on low-cost and preferably insulating substrates to allow the integral interconnection of solar cells. Major issues to be resolved include developing methods of "light trapping" to compensate for the reduced thickness of the silicon film and selecting a substrate that is not only low cost but also compatible with film deposition and processing. Approaches range from "lift-off" techniques using reusable, single-crystal substrates to epitaxial growth on low-cost metallurgical-grade silicon wafers to recrystallizing amorphous or small-grained films (either by melting or in the solid phase).

Table 2 Are There Enough Materials for Energy-significant PV Production?

Technology	Material	World Production (MT/yr)[a]	Materials Required (MT)[a,b]	% of Current Production	Annual Growth Needed (%)
Crystalline silicon	Purified silicon	25,000[b]	130,000	520	3.7[c]
	Silver (grids, cell pads)	20,000	6,000	30	0.53
Thin-film Cu (In, Ga)Se$_2$ alloys	Indium	250 (by-product)	400	160	2.0[d]
	Selenium	2,200	800	36	0.6[e]
	Gallium	150	70	47	0.9[f]
Thin-film CdTe	Tellurium	450 (2,000 unused by-product)	933	38 (of total, including unused)	2.2
	Cadmium	26,000 (by-product)	8	3	0.06
Thin-film silicon	Germanium	270 (3,200 unused by-product)	40	1 (of total, including unused)	0.7

[a] Necessary production for each type of PV technology to produce 20 GW/yr by 2050
[b] Metric tons
[c] Elemental silicon is not constrained by supply; current production is low because of low demand.
[d] Indium is a by-product of zinc, which has been growing at 3%/yr for 50 years. Indium growth will probably exceed demand because of growth in zinc.
[e] Selenium is a by-product of copper; an increase of only 0.16% per year would keep pace with demand.
[f] Gallium is not constrained by supply; current production is low because of low demand.

Transparent Conducting Oxides. Transparent conducting oxides (TCOs) play an important role in all thin-film solar cells. The key properties for high-quality TCOs are high optical transmission (high band gap for window materials), low electrical resistivity and high carrier mobility, low surface roughness (for most devices), good thermal and chemical stability, good crystallinity (for most devices), adhesion and hardness, and low processing cost. Typical processes used to fabricate TCOs include chemical and physical vapor deposition, sputtering, laser ablation, spraying, and solution growth (e.g., chemical bath deposition). Some commonly used n-type TCOs include indium tin oxide (ITO) and SnO_2 (both available commercially coated on glass), ZnO, and cadmium stannate (Cd_2SnO_4). Developing p-type TCOs is an important goal, because it would open up more possibilities for thin-film device structures, particularly multijunction devices. Materials being investigated include $CuAlO_2$, $CuInO_2$, $CuSrO_2$, and (N, Ga)-doped ZnO.

Concentrators

The key elements of a concentrator PV system are low-cost concentrating optics, low-cost mounting and tracking systems, and high-efficiency (and relatively low-cost) solar cells. The large-scale manufacturability of all components has already been demonstrated, including 27%-efficient silicon cells (up to 400 suns concentration) and 28%-efficient GaAs cells. Concentrator systems using point-focus Fresnel lenses (up to 400 suns) have been routinely fabricated. Module efficiencies of up to 20% have been demonstrated by commercially made 25%-efficient silicon solar cells. Recent progress in multijunction, III-V-based solar cells for space applications has led to looking at their terrestrial potential in concentrating applications. An efficiency of 37.3% (at up to 600 suns intensity) has been achieved recently for a GaInP$_2$/GaInAs/Ge triple-junction structure (King et al. 2004).

Most of today's remote and distributed markets for PV systems are not suitable for concentrator systems. Concentrator systems use only direct (rather than diffuse or global) solar radiation; therefore, their areas of best application are more limited than those for flat plates (e.g., in the southwest United States). A brief summary of ongoing research in silicon and III-V-based concentrator cells is provided below. There is also ongoing research to improve the long-term reliability of concentrator systems and to develop standard tests for concentrator cells and systems.

Silicon Concentrator Cells. To achieve the highest efficiencies, the cells are generally fabricated on float-zone silicon wafers. For concentrations of less than about 30 suns, the grid design of the 1-sun cell may be modified by increasing the number of grid lines to reduce series-resistance losses. Prismatic covers can divert sunlight away from the grid lines to mitigate the loss of photocurrent from high grid coverage. For high concentrations (>200 suns), the back-point-contact silicon cell (Mulligan et al. 2004) has a higher efficiency, partly because of no grid obscuration. Another approach is to fabricate "dense array" modules for use in reflective dish concentrators. These consist of interconnected silicon concentrator cells on single wafers, with several wafers connected in the module (typically 25 × 25-cm size).

Multijunction Concentrator Cells. The devices with highest efficiency are based on III-V materials, consisting of crystals grown from the elements within groups III and V of the periodic table, such as gallium, indium, palladium, and arsenic. Solar cells based on III-V materials are usually grown by metalorganic chemical vapor deposition (MOCVD) or by molecular beam epitaxy (MBE). Growth by MOCVD is typically accomplished between 600 and 700°C with a growth rate of 1-10 μm/hr. Growth temperatures and growth rates for MBE are usually somewhat lower. Both growth methods use a single-crystal substrate as a template for the epitaxy. For easiest growth, the substrate has a lattice constant that is equal to that of the desired epitaxial layers (i.e., lattice-matched). However, lattice-mismatched (or "metamorphic") structures are also used, as these allow combinations of band gaps that can be better optimized to the solar spectrum.

The configuration of the record-efficiency, three-junction device is Ga$_{0.44}$In$_{0.56}$P/Ga$_{0.92}$In$_{0.08}$As/Ge. The solar cell structures include the active *p-n* junctions,

passivating window and back-surface-field layers on either sides of the *p-n* junctions, and contacting layers to ensure low resistance contacts to the rest of the circuit. This includes very highly doped shorting (tunnel) junctions between the subcells of the multijunction device.

Growth of III-V solar cells on silicon has also been demonstrated, but these cells usually show inferior crystal quality compared with growth on GaAs or germanium. Recently, the first lattice-matched III-V-on-silicon tandem cell has been demonstrated, with GaNPAs (1.7 eV) as the top cell (Geisz et al. 2004).

Achieving 40% and greater efficiencies is being pursued by several groups worldwide. One approach is the use of 2–3% nitrogen in $Ga_xIn_{1-x}As_{1-y}N_y$ to reduce the band gap to about 1 eV (for the third junction in a four-junction device). Although 1-eV GaInAsN can be grown lattice-matched to GaAs, the addition of nitrogen degrades the electrical quality of the GaAs, thus far preventing the realization of a higher efficiency with a four-junction design. Other potential 1-eV materials are also being investigated. The use of five- or six-junction cells reduces the amount of current per junction and provides a pathway for GaInAsN to be a useful addition.

As for other III-V devices, commercial deposition systems are available for growing these multilayer devices with film thickness uniformities within <1%. Three-junction solar cells based on GaInP/GaInAs/Ge are commercially available for space applications. The efficiencies of these cells approach 30% under 1-sun, AM0 (space) conditions. If one were to convert the production of space cells today (a few hundred kilowatts annually, used with no or very low concentration in space) to terrestrial concentrator applications at 500–1,000 suns, the terrestrial output of these cells would be several hundred megawatts in concentrator systems. To date, multijunction cells have not contributed to the terrestrial PV market, and, at least in the near term, progress in these high-efficiency solar cells will continue to be driven by growing space-power markets.

NEW TECHNOLOGIES

Dye-sensitized Solar Cells

The dye-sensitized solar cell (O'Regan and Grätzel 1991) has foundations in photochemistry rather than in solid-state physics. In this interesting device, also called the "Grätzel cell" after its Swiss inventor, organic dye molecules are adsorbed on a nanocrystalline titanium dioxide (TiO_2) film, and the nanopores of the film are filled with a redox electrolyte. The dyes absorb solar photons to create an excited molecular state that can inject electrons into the TiO_2. The electrons percolate through the nanoporous TiO_2 film and are collected at a transparent electrode. The oxidized dye is reduced back to its initial state by accepting electrons from the redox relay via ionic transport from a metal counter-electrode; this completes the circuit and electrical power is generated in the external circuit. Dye-sensitized solar cells are extremely attractive because of the very low cost of the constituent materials (TiO_2 is a common material used in paints and toothpaste) and the potential simplicity of their manufacturing process. Laboratory-scale devices of 11% have been demonstrated, but larger modules are less than half that efficient. Stability of the devices (e.g., dye materials and electrolyte) is an ongoing research issue.

Organic and Nanotechnology Solar Cells

Organic semiconductors hold promise as building blocks for organic electronics, displays, and very low-cost solar cells. In an organic solar cell, light creates a bound electron-hole pair, called an exciton, which separates into an electron on one side and a hole on the other side of a material interface within the device. One result of this different "physics" is that organic solar cells can be about 10 times thinner than thin-film solar cells. Consequently, organic solar cells could lower costs in four ways: low-cost constituent elements (e.g., carbon, hydrogen oxygen, nitrogen sulfur), reduced material use, high conversion efficiency (the most critical issue for this technology), and high-volume production techniques (e.g., high-rate deposition on roll-to-roll plastic substrates). Research examples in organic solar cells include quantum dots (a nanotechnology) embedded in an organic polymer, liquid-crystal (small-molecule) cells, and small-molecule chromophore cells. Solar cell efficiencies to date are low (<3–5%). Nanotechnology for PV is exciting because the optical and electronic properties of the materials can be tuned by controlling particle size. They may be easy to manufacture when the nanoparticles are produced by means of chemical solution. Some of these concepts are already being pursued commercially. Long-term stability of these devices is another major issue to be resolved.

Storage and Distribution Costs

We note that none of the above discussion considers the costs of storage of the energy but instead assume a free electrical grid. The current grid can only handle at most 20% of its input power as intermittent power; hence, if solar electricity were to be used on a very large scale, the grid costs should also be included in the total adoption costs. In addition, for solar energy to play a role other than a fill for another baseloaded energy source, storage and transmission must be done on a large scale and cost-effectively. At present, the primary focus on solar electricity is on intermittent power production, but its widespread use as a primary power source will require equal attention to obtaining cost-effective storage and/or global distribution technologies to provide the power to the end-user on demand as opposed to when the solar resource is locally available to the conversion device.

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SOLAR FUELS

There are currently two solar fuels technologies in use for which performance and economic assessments are possible. These are biomass-derived fuels and hydrogen produced by electrolysis. In the latter case, electricity is derived principally from fossil fuel sources, which ultimately derive from biomass as well.

The state of biomass-derived fuel production is reviewed in the first part of this assessment, while the second portion describes the state of the research effort to produce hydrogen fuel using electrolysis.

BIOMASS-DERIVED FUELS

Biomass is the oldest form of solar energy to be used by humanity. Until about 1800, biomass was the predominant fuel used for heating, metallurgy, lighting, and transportation (as animal fodder), as well as supplying materials needs in the form of timber and fiber and, of course, as food for human sustenance. The energy use of biomass is primarily from the 14.9-Gha terrestrial surface of the Earth, of which only 56% is productive terrain with forests, savannas, prairies, and arable land.

The current biomass primary energy (bioenergy) supply is about 11% of the total energy demand of 13.3 TW (IEA 2004), or 1.4 TW. Human food intake for metabolic needs is around half that at about 0.65 TW. The industrial country use pattern is for heat and electricity (very often in combined heat and power [CHP]) using mainly solid biomass, along with a growing use of liquid fuels such as ethanol and biodiesel produced from crops (Chum and Overend 2003). The capture of methane from environmental technologies, such as anaerobic digestion, is also widely practiced (Schulz and Eder 2001).

The developing country pattern is more artisanal and inefficient; biomass is often used as fuelwood in cook stoves and to provide energy in small-scale industries (tea-drying, brick kilns, charcoal manufacture, etc.) The major development areas for biomass-to-fuels are concerned with the production of liquid fuels such as ethanol; electricity and co-produced heat; gaseous fuels such as methane, fuel gas, and syngas; and in the future, hydrogen. The United States has a major program to develop processes that co-produce energy and higher value products, such as biorefineries (DOE 2003).

The large scale of the biomass and bioenergy supply chain is set in a framework of constraints with respect to the environment, food and fiber supply, and sustainability. Most of the biomass used in industrial countries is part of a cascade of use, reuse, and recycling of biomass materials with post-consumer residues being very important, along with the use of residues generated on farms, in the forest, and in the industries that process biomass.

However, crops for energy are of growing importance as sugar cane (Goldemberg et al. 2004), cereals (Bullion 2004), and oilseeds (Martini and Schell 1998) become significant inputs to the expanding liquid biofuels markets. These tend to be the most expensive biomass resources,

currently accounting for only a small proportion of the supply curve. This is changing and in many respects, the biomass industries of today are, in fact, renewable carbon managers — gaining the maximum utility from these residual streams prior to the return of the carbon as CO_2 to the atmosphere.

The bioenergy potential is the subject of much debate due to the limited land area and the competition that is perceived with the food and fiber sectors. A summary of recent projections for the biomass primary energy supply suggests a potential range between 1 and 40 TW (IEA 2004a). The central value is about 14 TW. Assuming liquid fuel production at today's 40% thermal conversion efficiency, this would produce 80 million Bbl/day of refined products.

Biomass Supply Issues. Given that most of today's biomass is derived from cascading, it is useful to look at the biomass material flows, as shown in Figure 68. At the terminal ends, the majority of biomass today is used to provide energy services mainly as heat, and the technical term used by the combustion engineering profession is that these fuels are *opportunity fuels* (Tillman and Harding 2004) — thus, much of the biomass conversion technology consists of adaptations of fossil fired units, including coal, oil, and gas.
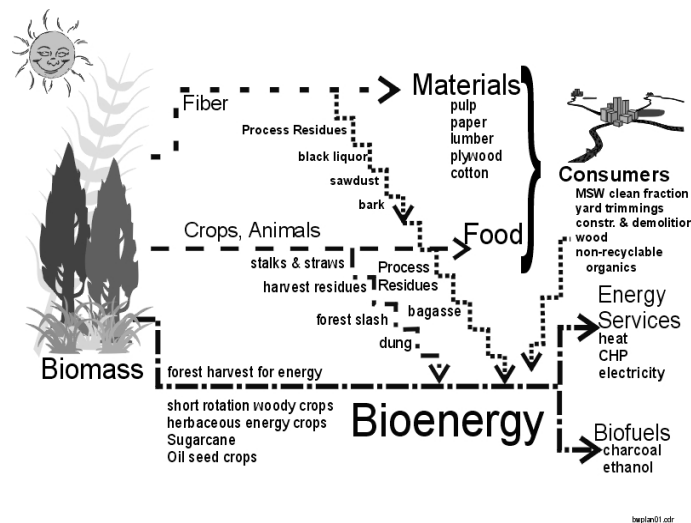
Figure 68 Biomass material flows

Estimating future biomass supply has proved to be rather complex. There are basically four different approaches to establishing the biomass resource:

   (1) Biomass surveys at a fixed point in time;

   (2) Estimation of residues, using two parameters — the actual production of the desired crop or product and residue factor that is empirically derived from measurement of, say, the corn stover and cob mass in relation to the yield of corn;

(3) Resource inventories (which can be performed through remote sensing supported by statistical means from so-called ground truth) maintained on a continuous basis (Parikka 2004), and

(4) The Agro Ecological Zone (AEZ) methodology based on advances in remote sensing, and the ability to model crop growth (Fischer et al. 2005).

Figure 69 shows the trend in biomass utilization for energy in the United States since before the 1973 energy crisis, which stimulated a wide range of measures to utilize more biomass in the energy system. Note that the data for electricity generation were not available from non-utility biomass users until five years ago; prior to that period, the electricity generated was lumped together with the industrial heat (CHP) generation (EIA 2000).
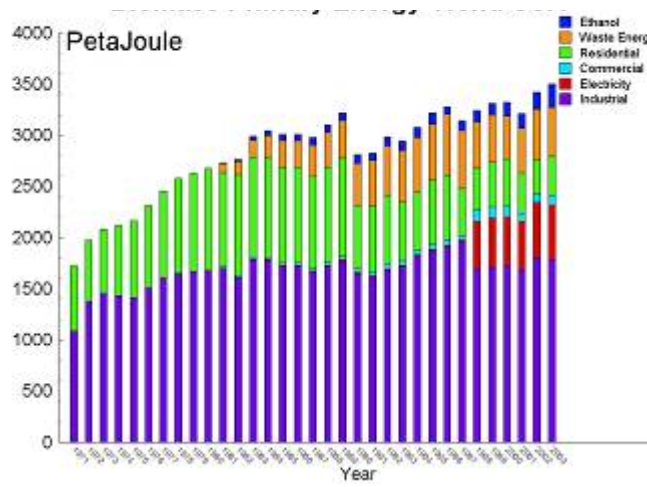
Figure 69 Biomass primary energy trend for the
United States (Source: EIA 2000)

Combustion

With the exception of the production of biofuels such as methane in anaerobic digestion, and ethanol or biodiesel, most biomass today is utilized in solid form and burned directly to produce heat and/or electricity. The scale of biomass combustion devices ranges from less than 1 kWth in developing country domestic cook stoves, to over 300–500 MWth input in the largest industrial CHP units.

In the last two decades there has been an increasing use of biomass as a co-fire fuel in large utility scale boilers fired with coal. While this option does not increase the availability of electric power, it does provide offsets to both carbon dioxide and sulfur emissions, and has been demonstrated to have very little effect on the overall efficiency of the coal boiler, up to 10–15% biomass energy substitution in an individual combustion unit. The higher efficiency in this use is often accompanied by better emissions control than with biomass-only fired units

Anaerobic Digestion

One gasification process that has reached widespread application is the use of biogas, a mixture of methane and carbon dioxide produced in anaerobic digestion processes. This occurs naturally in landfills and in the last few decades, landfill gas (LFG) has not only been collected for use (for safety and environmental reasons), but has also become a major source of renewable electricity generation in Europe and the United States. There is approximately 1 GW of installed LFG capacity in the United States, with units ranging from hundreds of kilowatts to 50 MW. There are also industrial-scale constructed anaerobic digesters for urban residues, which have much shorter residence times than landfills (operating at 35ºC and 50ºC, rather than the ambient ground temperature), as well as increased resource recovery potentials (IEA 1998).

Liquid Fuels and Hydrogen

The only way to decarbonize light-duty vehicle fuels (about one-third of U.S. energy use) is to remove the fossil carbon by (1) changing to electricity or hydrogen produced from non-carbon sources, (2) using fossil fuel processes, which capture and sequester the carbon dioxide, or (3) replacing the fossil carbon with renewable carbon. Decarbonization constitutes a major research direction for biomass programs. The major biomass-derived fuel is ethanol produced from sugars in Brazil, and from starches in the United States and Europe.

Three countries — Brazil, the United States, and India — account for nearly 90% of the world's ethanol production from biomass (using sugar cane and cereals). Current world ethanol production is about 0.02 TW. The total production was 21 metric tonnes in 2002 (FAOSTAT 2001) and the rapidly growing U.S. amount was 6.1 metric tonnes in that year. The U.S. statistics up through 2004 are shown in gasoline gallons equivalent and also as a fraction of the total corn (*Zea maize*) consumption.

Potentially, the ethanol yield in either process could be increased by 10–20% by converting residual starch and the hemicellulose and cellulose in the remaining corn solids to ethanol. Other development efforts involve higher-value by-products. The industry has demonstrated a very significant learning curve in the past 25 years, reducing the energy consumption within its processes, increasing the yield of ethanol, and significantly reducing the capital investment to levels approaching 1.00 $ annual gallon production capacity (IEA 2004). Typical dry mill plant sizes are about 40–50 million gallons year (IEA 2004); such mills are increasingly being constructed by farmers' cooperatives in the grain-growing areas to reduce the costs of corn transportation.

Lignocellulosics to Ethanol by Means of Bioconversion

One method of converting biomass to biofuels is depolymerization of the cellulose and hemicellulose into their component sugars, followed by bioconversion of those sugars to the fuel. Multiple methods of cellulose and hemicellulose depolymerization have been researched. Those methods include chemical treatments, biological enzyme treatments, and combinations of the two. The combination that has received the most research funding and analysis is dilute-acid

hydrolysis of the hemicellulose, followed by enzymatic hydrolysis of the remaining lignocellulose complex (Aden et al. 2002). Using only the experimentally achieved process parameters and a feedstock cost of $53/dry ton, the calculated minimum ethanol selling price (MESP) is $2.70/gal. The major barrier issues that are being addressed in the research and development (R&D) programs are optimal composition of the biomass, hemicellulose decomposition, recalcitrance of cellulose, fermentation strain robustness, and lignin utilization. Taken together, the future MESP is forecast to be similar to that of corn ethanol.

Thermochemical Conversion of Lignocellulosics to Fuels

Thermochemical routes involve gasification of the biomass to a syngas followed by catalytic conversion of the syngas (H_2 + CO) to produce fuels. Another process involves pyrolysis of the biomass to produce an oil that can be steam-reformed to synthesis gas for the production of liquid fuels. Unlike the biological processes above, thermochemical routes are indifferent to the polymeric composition of the materials; they utilize all of the carbon in the conversion, and build on over a hundred years of conversion of solid fuels in coke and town gas works.

Syngas has been produced since the 1930s from coal or petroleum coke gasification, and its conversion to hydrogen and Fischer-Tropsch (F-T) liquid (FTL) hydrocarbons and waxes has also been achieved at a commercial-scale (Courty et al. 1999). Presently, there are many natural gas-to-liquids projects based on FTL using remote and shut-in gas resources through either steam-reforming or partial oxidation technology. FTL hydrocarbons have an Anderson, Shultz, and Flory (ASF) distribution of carbon chain length with degree of conversion over the catalyst. Recent advances in the area have allowed the production of high chain lengths (waxes) which are then hydrocracked to the fuel product. Mixed alcohols can also be produced over F-T-like catalysts, again with an ASF distribution, however, by recycling the methanol (a C_1 product), the yield of ethanol is increased together with mixed alcohol products having economic values that are much greater than their values as fuels.

If a plant to produce hydrogen from biomass via syngas were to be built today and the catalysts were demonstrated to have a long life, the minimum hydrogen selling price is estimated to be $1.38/kg, with an intermediate syngas price of $6.88/GJ (Spath and Dayton 2003).

HYDROGEN FROM ELECTROLYSIS OF WATER

Less than 1% of the hydrogen produced in the United States is made with electrolyzers running off of grid power generated using carbon-based fuels. The bulk of hydrogen production is done through the steam-reforming of natural gas for use in fertilizer production, and this gas is too impure to be used in the fuel cells envisioned for transport vehicles. As a result of the recent focus on a hydrogen economy, many studies have been made of the present status of this small market technology for electrolytic hydrogen production. Elements of these analyses (Ivy 2004; NRC and NAE 2004; DOE 2004) are presented here to provide a reference point for solar hydrogen production.

Electrolysis is the process for breaking water into its constituent elements of hydrogen (H_2) and oxygen (O_2) gas by supplying electrical energy. The advantage of the process is that it supplies a very clean hydrogen fuel that is free from carbon and sulfur impurities. The disadvantage is that the process is expensive relative to steam-reforming of natural gas, because of the cost of the electrical energy required to drive the process.

Several reasons argue in favor of hydrogen as a chemical fuel and electrolysis as a means of making this hydrogen fuel (NRC and NAE 2004). Water, and the hydrogen that it contains, is more abundant than hydrocarbons and is available wherever there is practicable human habitation. Electrolysis also represents a means to convert fuels such as coal into a higher-value fuel for transport. In addition, the electrolysis technology can be scaled over a broad range of distributed applications, from existing fueling stations for automobiles, to high-volume, centralized hydroelectric or nuclear power plants. Electrolysis also represents a way to transform the electrical power generated from renewable sources such as hydro, wind, or solar into a fuel.

Electrolysis technologies have been in use for decades to meet industrial chemical needs. They have also played a critical role in life support in space and submarine applications over the past decades. Presently, however, commercial electrolyzers for production of hydrogen are commercially viable only in niche industrial applications. They are sometimes employed at isolated locations where there is no available natural gas for production of fertilizers. There are also small distributed market demands for limited amounts of hydrogen at truckload quantities, where the customers absorb the high $12/kg cost of electrolytically produced material. In contrast, the U.S. Department of Energy (DOE) estimates that in order to compete for transportation fuels, cost of hydrogen must be pushed below $3.00/kg, where a kg of hydrogen is seen to power an automobile for 60 miles of travel.

Electrolyzers for production of hydrogen fall into two basic categories: solid polymer and alkaline liquid electrolyte. The difference in technologies also defines a difference in scale of application: the alkaline electrolysis units can be scaled up to high-volume production, whereas the solid polymer technology is best suited to small-volume production.

Solid polymer electrolyzers are also referred to as proton exchange membrane (PEM) electrolyzers. General Electric and other companies developed this technology in the 1950s and 1960s to support the U.S. space program. When water is introduced into the PEM electrolyzer cell, hydrogen ions are drawn into and through the membrane, where they recombine at the cathode with electrons to form hydrogen atoms. Oxygen is produced at the anode on the other side of the membrane from the hydrogen and is removed as the water is recirculated.

Alkaline industrial electrolysis units are produced in two forms today, in a unipolar or bipolar form, which describe a parallel or series connections of the electrodes used in the electrolysis. Both, however, utilize aqueous potassium hydroxide solutions. An ion exchange membrane is placed between the cathode and anode, separating the hydrogen and oxygen as they are produced, but allowing the passage of ions between the two sides.

Both technologies are governed by the same electrolysis reaction:

$$H_2O \rightarrow \tfrac{1}{2} O_2 + H_2 \tag{1}$$

At the PEM system electrodes, this reaction scheme breaks up into two half-reactions:

<div align="center">

Cathode PEM Hydrogen Production

</div>

$$2\ H^+ + 2e^- \rightarrow H_2 \tag{2}$$

<div align="center">

Anode PEM Oxygen Production

</div>

$$H_2O \rightarrow \tfrac{1}{2}\ O_2 + 2\ H^+ + 2e^- \tag{3}$$

The alkaline systems differ in the components of the reactions scheme:

<div align="center">

Cathode Alkaline Hydrogen Production

</div>

$$2\ H_2O + 2e^- \rightarrow H_2 + 2\ OH^- \tag{4}$$

<div align="center">

Anode Alkaline Oxygen Production

</div>

$$2\ OH^- \rightarrow \tfrac{1}{2}\ O_2 + H_2O + 2e^- \tag{5}$$

Process Diagram

The overall process for the production of hydrogen gas is depicted in the process diagram shown in Figure 70, where the input of process water results in an output of compressed hydrogen to a storage tank.

Not all of the commercial water electrolyzers mentioned above contain all of the elements of this process. Some units lack water deionizers or reverse osmosis purification units, and others do not have compressor units that can attain the 6,000 psi pressure required for hydrogen storage. The
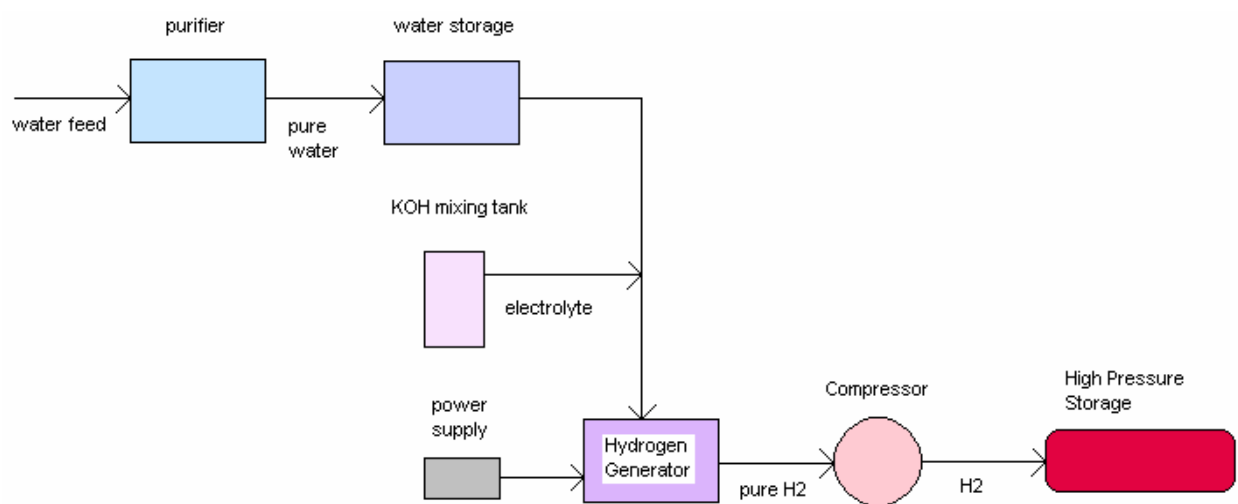
Figure 70 Process flow diagram (Source: Ivy 2004)

alkaline electrolyzers require a mixing tank for KOH, which the polymer electrolyzers do not. In the comparison of hydrogen production methods described below, adjustments in efficiency and cost numbers must be made for these differences.

State of the Technology

The state of the technology in electrolytic systems is summarized in Table 3, where the performance characteristics are listed for a representative array of commercial electrolysis systems (NRC and NAE 2004). The data in this table have been derived from Ivy 2004, and NRC and NAE 2004. The daily production of H_2 for these systems ranges from 10 kg to 1,000 kg. With the exception of the Proton product, all of the electrolyzers shown are alkaline systems.

In the Proton HOGON 380 PEM system, the highest conversion efficiency of electricity to molecular hydrogen is attained: 95% of the current flow results in the production of hydrogen from water. In the alkaline systems, a lower figure near 80% holds. The balance goes to side reactions. The overall system energy required to produce hydrogen ranges from 53.4 to 72.4 kWh/kg. These figures include the entire energy requirement for hydrogen production, including the electrolyzer, compressor, and the other ancillary equipment depicted in the process diagram shown in Figure 70. For the Stuart and the Norsk examples, the fraction of the system energy attributable to the electrolyzer is seen to run about 83–89%. The overall system efficiency is the energy stored as hydrogen per unit input of energy expended. This result utilizes the higher heating value for hydrogen of 39 kWh/kg.

Table 3 Performance Characteristics of Commercial Electrolyzers

Electrolyzer Brand and Model	H_2 Production (kg/day)	H_2/H_2O Product/ Reactant (%)	System Energy* (kWh/kg)	Electrolyzer Portion of System Energy (%)	Overall System Efficiency† (%)	System Power Requirement (kW)
Stuart IMET 1000	130	80	55.7	83	70	288
Teledyne EC –750	91	80	64.6	-	60	235
Proton: HOGON 380 (PEM)	22	95	72.4	-	54	63
Norsk Hydro type 5040	1040	80	53.5	89	73	2330
Avalence: Hydrofiller	11	89	62.8	-	62	25

* Includes a 2.3 kWh/kg adjustment for compression of the H_2 to 6,000 psi (NRC and NAE 2004).

† Assumes a higher heating value (HHV) of 39 kWh/kg for H_2.

Costs of Hydrogen Production with Carbon-based Fuels

Other carbon-based fuels can be transformed into hydrogen for use in the niche markets that have been mentioned previously. Electrical power serves as the intermediary between the two, with the energy losses inherent in the transformation contained within the resulting electrical power cost. Estimates of the cost of production of hydrogen through electrolysis are straightforward to make, although there are a series of assumptions that are involved. An example is given here (Ivy 2004) for three systems designed for different output levels: a small 20 kg/day output, a larger 100 kg/day level, and a very large 1,000 kg/day production. These systems span the range from a neighborhood, four cars per day output to a 1,000 kg/day fueling system servicing a couple of hundred cars per day.

The cost breakdown for hydrogen production in these scenarios is given in Figure 71 in 2005 dollars (Ivy 2004). All three levels have been derived using the same financial analysis for a 40-year system lifetime, which includes, among other considerations, a 7-year depreciation schedule, a common tax treatment, siting and labor costing, and maintenance, contingency, decommissioning, and insurance costs, much of which are proportionate to the total capital cost of the electrolyzer unit. Electrolyzer lifetimes range from 7 to 10 years before replacement. A final assumption is an industrial electricity cost of 4.83 cents/kWh, which is decidedly unrealistic for small-volume production, and is unlikely even at the 1,000 kg/day level.

The analysis reveals a cost that ranges from $4.15/kg to $19.01/kg. A similar National Academy of Engineering (NAE) analysis derives a cost of $6.56 for a 480 kg/day unit (NRC and NAE 2004). The cost of electricity is a driving factor in all three cases, with the capital costs of the small production units forming the major cost. If properly designed, the overhead and
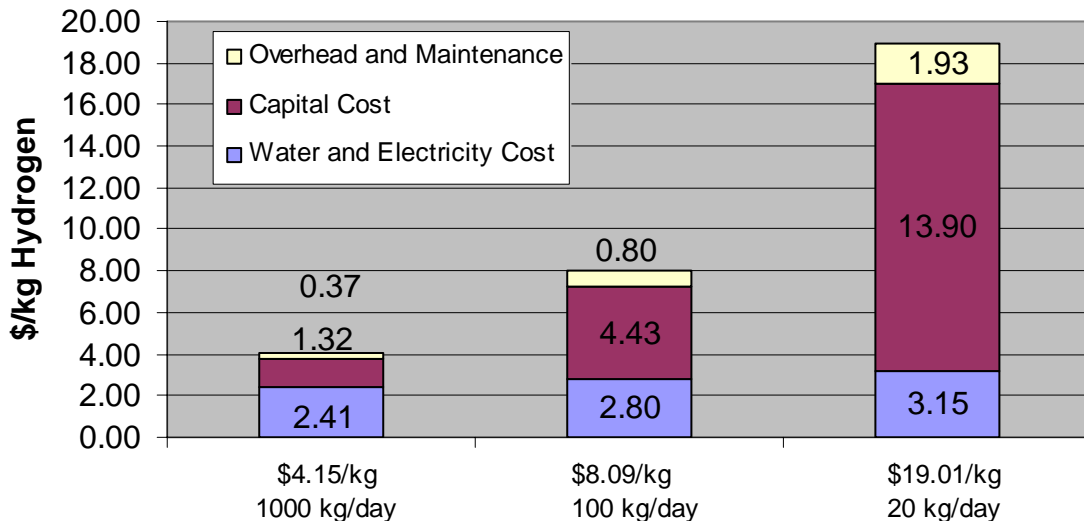
Figure 71 Hydrogen selling costs for carbon-based power (assumes price of $.0483/kWh)

maintenance costs of the small production unit could be minimized with a do-it-yourself owner. For the larger-sized units, electrical costs dominate the costing. Water is the other feedstock material and it appears not be a limiting factor. To run the current U.S. light-duty fleet with hydrogen would require 100 billion gallons/year, which is far smaller than the yearly domestic personal use of 4,800 billion gallons/year (Turner 2004).

This is how the market stands today. Electrolytic production of hydrogen represents a minute fraction of the market output of hydrogen and the economies of scale of production of the electrolyzer units have not yet come into play. The NAE, for example, works with projections of an eight- to ten-fold decrease in cost of the electrolyzer units for both alkaline and PEM technologies (NRC and NAE 2004). Of concern, however, is the purity of the water required for the electrolyzers. Water purification is a mature technology and there should be little economies of scale of this element of the electrolyzer system.

Part of this perceived reduction in cost involves advances in the design and efficiency of the membranes and catalysts in the two different technologies. The alkaline electrolyzers will utilize the well-known Raney nickel catalyst, about which much is known, both in terms of costing and performance. It is compatible with a low-cost system. The PEM technology, however, relies upon platinum catalysts for gas evolution, which is a scarce material. Given a practical $0.20–1.0$ mg/cm^2 loading level of Pt in a PEM, a typical generation current of 0.4 A/cm^2, and the hydrogen production efficiency in Table 1, a yearly production rate of 1 TW would require 170–850 metric tons of Pt. Even though recovery of Pt from these membranes can approach 98%, this required base of 170+ tons exceeds the 2005 annual global production of Pt of 165 tons. For comparison, the automotive industry utilizes about 62 tons of Pt annually. In this situation, the PEM power business would determine the market for platinum.

Costs of Hydrogen Production with Solar Electricity

It is useful to estimate the costs of hydrogen production using photovoltaic solar cells as a source of electrical power. In this case, the overall system of solar facility and electrolyzer must be optimized as a unit. Given the diurnal nature of solar insolation, the electrolyzer cannot be powered twenty-four hours per day, and the hydrogen output is decreased in a corresponding manner. The lowest price for hydrogen is obtained through an optimized balance of solar vis-à-vis electrolyzer costs. The Norsk Hydro 5040 electrolyzer unit from the 1,000 kg/day electrolyzer example above will run on 240–2,330 kW of power for operation (Ivy 2004). If this unit is powered with 2,330 kW of peak watt solar power, the daily variation in insolation will limit the overall production to 250 kg/day of hydrogen. This combination is near optimum for the lowest hydrogen cost. Over a forty-year period, at the present cost for photovoltaic solar cells of $6 per peak watt with balance of system costs, and including amortization, the price of hydrogen can be calculated and is shown in Figure 72 to be $17.78/kg. The capital cost of the electrolyzer is taken from Figure 71 with an adjustment for the decrease in daily hydrogen production and assuming constant system efficiency over the entire range of input electrical power. With improvements in solar technology by 2020 and a drop in solar cell costs to $1.5/W$_p$, the overall cost for hydrogen would drop to $8.68/kg.
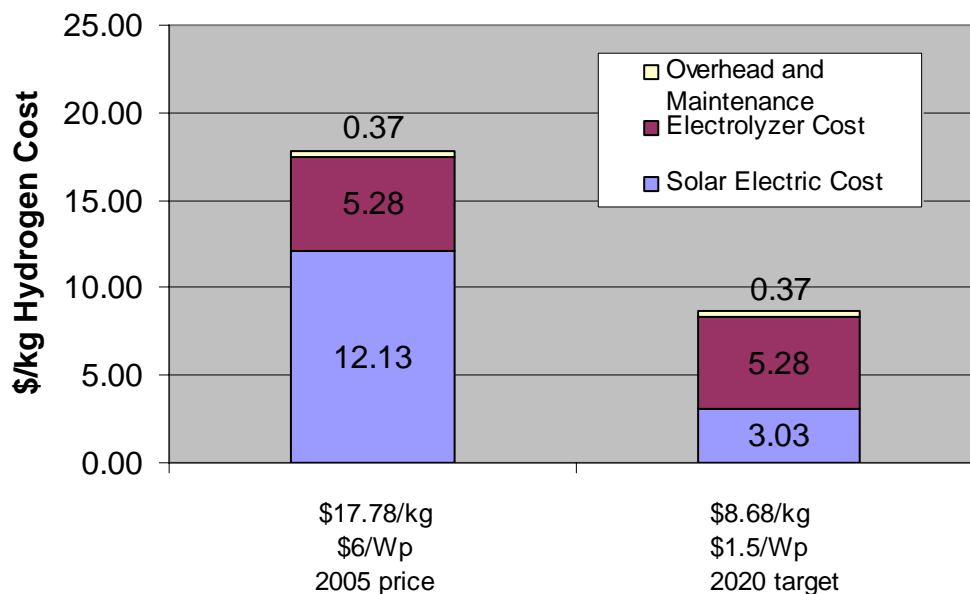
Figure 72 Hydrogen selling price for carbon-free solar electricity (assumes 42 kg/hour production rate)

This analysis reveals that the capital cost of the electrolyzer becomes significant in an application that combines it with solar power.

With a 2020 solar efficiency of 20% and an electrolyzer system efficiency of 65%, the overall solar conversion efficiency will be about 13%. It is not unreasonable to foresee that by 2020, systems for photocatalytic hydrogen evolution, where hydrogen is evolved directly from a photocatalytic surface, would probably be more effective than electrolyzers in generating hydrogen fuel.

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SOLAR THERMAL AND THERMOELECTRICS

THERMAL SYSTEMS

Solar thermal systems use solar radiation as a source of heat; this heat can be used in several ways. It can be used for climate control in buildings — heating and cooling. It can be concentrated to produce temperatures high enough to generate electrical power, and it can also be used in this concentrated mode to induce reactions to make chemical fuels. With focused solar radiation, photovoltaic (PV) devices can function at a much higher efficiency.

Low-temperature solar thermal systems do not involve sunlight concentration; they may occasionally employ low concentration at a factor of $C \leq 2$. The optical concentration of direct sunlight involved in power and fuel generation may range from about 20 to several thousand, depending on the specific process and system involved. Solar PVs are found at the higher end of this concentration range.

Innovations and new developments in solar thermal generally involve a significant reduction in cost or the introduction of a previously unattainable mode of operation.

Low-temperature Solar Thermal Systems

Based on recent U.S. Department of Energy (DOE) Annual Energy Outlook reports, residential and commercial buildings account for 36% of the total primary energy use in the United States, and 30% of the total U.S. greenhouse gas emissions. About 65% of the energy consumed in the residential and commercial sectors is for heating (46%), cooling (9%) and refrigeration (10%); in principle this energy can be provided by non-concentrating solar thermal systems. Based on population density and climate, 75% of U.S. households and commercial buildings are appropriate candidates for non-concentrating, solar hot water systems.

Initial cost is considered a major barrier to the increased use and market growth of solar hot water and heating systems. Improved performance and the use of low-cost materials are the best means for cost reduction. Recent R&D efforts have focused on polymer-based systems, which will be most cost effective when production capacity is scaled up. The progress of polymer system hinges on material development with specific requirements for glazing and heat exchangers — used to absorb incident sunlight and transfer solar energy to potable water. Needed development areas include materials that are durable and compatible with potable water, and design and manufacturing processes that take advantage of the cost savings potential of replacing glass and metal with plastics.

Concentrated Solar Thermal Processes for Power Generation

A good fundamental review of solar thermal power plants in general and concentrating methods used in solar thermal systems is provided by Winter et al. (1991). All power-generating solar thermal systems can be hybridized with fuel to supplement solar power during low-insolation

periods and extend the system operation beyond the solar hours. Fuel hybridization prevents direct normal irradiation (DNI) variations from adversely affecting the engine efficiency; therefore, hybridized solar systems typically have higher solar-to-electricity conversion efficiency and hence produce more solar power than similar nonhybrid systems. Various storage options can also be added to most solar thermal systems.

The three main components of a concentrated solar thermal system are (a) the reflector/concentrator that reflects concentrated light onto the aperture of a receiver positioned at its focus, (b) the receiver that converts the radiation to heat (or chemical potential), and (c) the engine that converts heat to electricity. The power conversion efficiency η_{PC} is the product of the receiver and engine efficiencies:

$$\eta_{PC} = \eta_{rec}\,\eta_{eng}. \tag{1}$$

Figure 73 demonstrates the characteristics of solar thermal conversion efficiency by showing the variation of ideal system efficiency with temperature and sunlight concentration. The ideal receiver efficiency, assuming no losses in the optical concentration component and negligible conduction and convection losses, is

$$\eta_{rec} = 1 - \sigma(T_H^4 - T_L^4)/IC, \tag{2}$$

where

σ = Stefan-Boltzmann constant

T_H = effective receiver reradiation temperature

T_L = ambient temperature

I = flux (or intensity) of the DNI at design conditions

C = sunlight concentration ratio.

The limiting efficiency of a heat engine is given by the Carnot expression for the ideal engine:

$$\eta_{eng} = 1 - T_L/T_H. \tag{3}$$

In this simplified ideal case, the upper engine temperature is assumed to be equal to the effective receiver reradiating temperature.
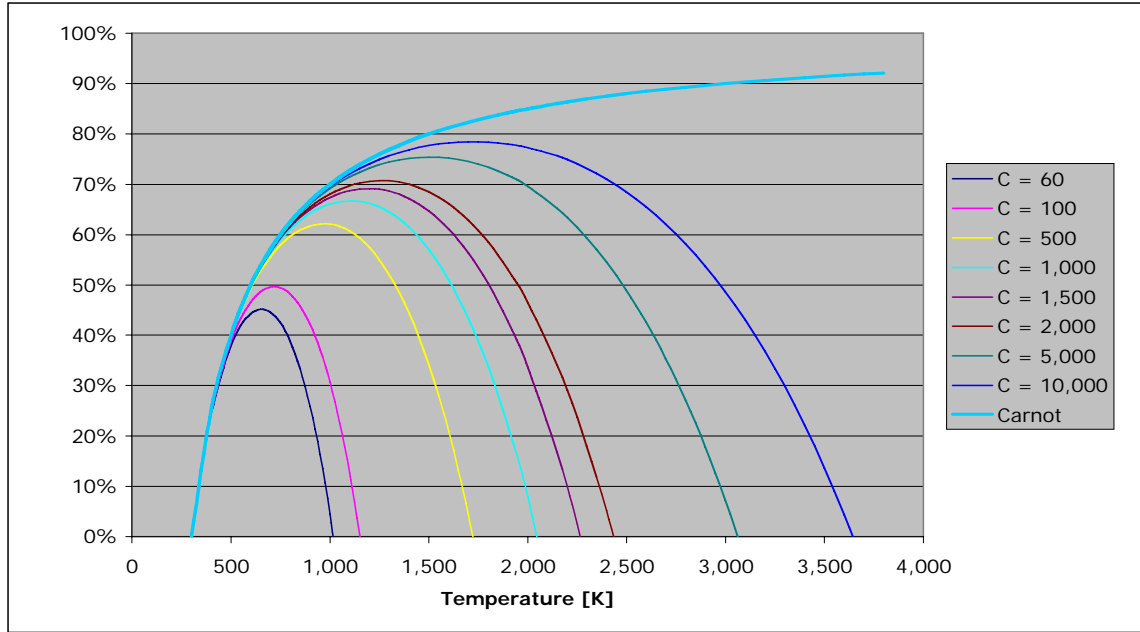
Figure 73 Variation of ideal power conversion efficiency of a solar thermal system with temperature and sunlight concentration ratio; assumed DNI = 1000 W/m^2 [after Fletcher and Moen (1977)]

As shown in Figure 73, ideally, the power conversion efficiency of solar thermal systems increases with temperature and concentration. However, the overall efficiency of a real system depends also on the optical efficiency; that is:

$$\eta_{sys} = \eta_{opt}\, \eta_{rec}\, \eta_{eng} \;. \tag{4}$$

Here the optical efficiency η_{opt} is the ratio between the solar radiation reaching the receiver aperture (i.e., the "target") and the direct normal solar radiation approaching the reflector/concentrator collection area.

After some simplification, the optical efficiency becomes

$$\eta_{opt} = \rho^n\, (1 - Sp)(1 - Sh)(1 - Bl) \;, \tag{5}$$

where

ρ = reflectivity of optical components

n = number of reflections

Sp, Sh, Bl = spillage (including back reflection), shadowed, and blocked portions of the incoming sunlight, respectively.

215

When $\eta_{opt} < 1$, Equation (2) becomes

$$\eta_{rec} = 1 - \sigma(T_{R,H}^4 - T_L^4)/IC\eta_{opt}.\tag{6}$$

This is the receiver efficiency when conduction and convection losses are negligible. The engine efficiency must account for actual losses in its various components and the generator efficiency. Equation (3) therefore becomes

$$\eta_{eng} = (1 - T_L/T_{E,H})(1 - L_{eng})\eta_{gen},\tag{7}$$

where

L_{eng} = combined fraction of all the component and parasitic losses

η_{gen} = generator efficiency.

Note that in a real system, the effective receiver reradiation temperature $T_{R,H}$ and the upper engine temperature $T_{E,H}$ are usually not the same.

An expression for real system efficiency is obtained by introducing Equations 5, 6, and 7 into Equation 4.

Typically, as the engine size increases, η_{eng} also increases, and its specific cost (dollars per kilowatt) is reduced. On the other hand, the high concentration required to maintain high power conversion efficiency during operation at high temperatures (Figure 73 and Equations 1, 2, and 3) is more difficult to attain in large systems, and it is associated with optical efficiency reduction. This difficulty is compounded by the continuous change of the sun's location, which causes the annual-average components and system efficiencies to be significantly lower than the respective design point efficiencies. Innovations that could alleviate or resolve the apparent mismatch between the optimum size and configuration of the optical and power conversion components in a solar thermal system are vital in achieving the cost reduction required for competitiveness.

The traditional approach of the solar community has been that large-volume production is the key to cost reduction. Although this might be true, the development and utilization of lower-cost materials, implementation of more efficient methods, and improvement of key components can also lead to significant cost reduction.

Three optical configurations developed for concentrated solar thermal systems are as follows: line focus systems, central receiver systems, and on-axis tracking systems.

Line Focus Systems. In line focus systems, sunlight is "folded" in one direction — from a plane to a line. In most cases, the optical configuration is that of a trough tracking the sun from east to west and a target that rotates accordingly (see Figure 74); recently, linear Fresnel reflectors with stationary target have also been used (Mills et al. 2004). The heat transfer fluid is heated in the tubular receiver. It then provides thermal energy to drive a Rankine cycle and
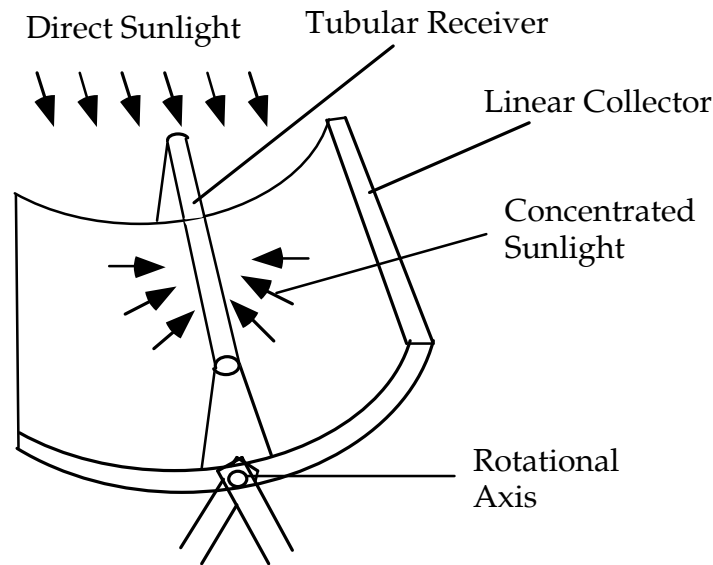
Figure 74 Trough (line focus) system configuration

generate electricity. The main inherent advantage of the system is its compatibility with large engines (i.e., steam turbines of hundreds of megawatts). The main inherent disadvantage is the low operating temperature, limited to less than 750K by the relatively low concentration and long tubular receiver configuration.

About 350 MW of capacity, generated by trough systems, was installed in California in the 1980s and early 1990s and has been continuously improved (Price et al. 2002). Recent developments have focused on means to increase operating temperature and/or reduce components and electricity cost. These include optical improvements with new concepts (Mills et al. 2004) and new designs to reduce optical losses in trough systems (Herrmann et al. 2004). Receiver efficiency can be enhanced by developing selective coatings capable of reaching higher temperature and by introducing smaller and more durable glass-to-metal seals and connections between receiver pipes (Benz and Kuckelkorn 2004). Working fluids and heat transfer means can be improved by direct steam generation in the trough (Almanza et al. 2002) or through the use of molten salt as working fluid. Thermal storage can be introduced by using solid materials (Laing et al. 2004) or high-heat-capacity fluids and phase-change materials (Tamme et al. 2004).

Central Receiver Systems. Central receiver systems are fundamentally Fresnel reflector arrays where the reflectors (heliostats) have two axes of rotation and their common focus is stationary, at the top of a tower (see Figure 75). The two-axis tracking enables higher concentration ratios and higher operating temperatures than those of the line focus configuration, but as the system size increases, the optical efficiency declines and this advantage is diminished. The power conversion unit of large central receivers (20–200 MW) is likely to be a steam Rankine turbine, while smaller central receivers can accommodate Brayton and combined cycles operating at higher temperatures. Increasing the temperature generally leads to higher power conversion efficiency but lower optical efficiency; thus, system optimization is required.
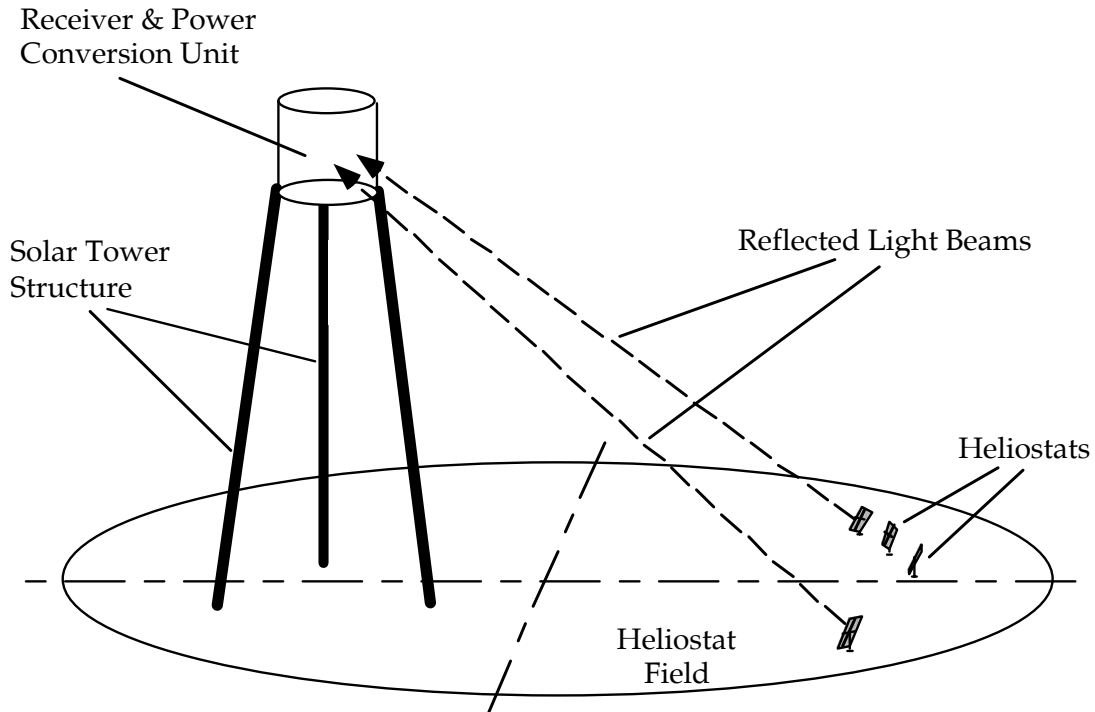
Figure 75 Central receiver (solar power tower) system configuration

Several power conversion methods have been developed for solar central receivers. A 10-MW system using molten salt as heat transfer fluid and storage medium, combined with a steam Rankine turbine at up to about 850K was demonstrated in the DOE Solar II project. Other methods are (a) steam generation and superheating in the receiver, (b) heating of atmospheric air to about 950K in the receiver and then using it to superheat steam, and (c) heating of compressed air in the receiver to over 1,100K and using it in a solar/fuel hybrid gas-turbine.

On-axis Tracking Systems. On-axis systems, such as the parabolic dish concentrators depicted in Figure 76, provide the highest optical efficiency of all the concentrating solar systems. Their main drawback is the concentrator size, which is limited by practical structural considerations; dishes with reflective area of 15–400 m^2 have been built and tested. Much of the development of on-axis systems involved the use of solarized Stirling engines for power conversion. Recent progress in small Brayton engine development provides the option of using a dish/Brayton system as an alternative to the dish/Stirling system.

Recent advancements related to central receivers and on-axis tracking systems focus on improving performance and reducing the cost of the concentrator (heliostat or dish) by increasing the reflector size and working with low-cost structures, better optics, and high-accuracy tracking. Optical efficiency has been increased by means of nonimaging secondary concentration (Welford and Winston 1989; Ries et al. 1997a), improved tracking methods, and better optical system design software. New "directly irradiated" or "volumetric" receivers have been found
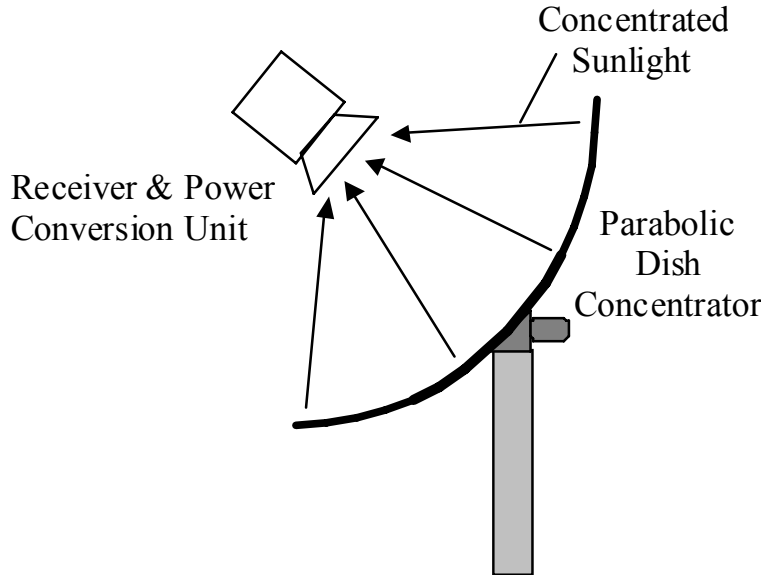
Figure 76 On-axis (parabolic dish concentrator) system configuration

that can operate efficiently at high solar fluxes and in temperature and pressure ranges compatible with those of advanced heat engines (Bertocchi et al. 2004; Karni et al. 1997). Enhanced radiation and convection heat transfer have been obtained by developing high-temperature ceramic absorbers for the solar receiver (Karni et al. 1998; Fend et al. 2004).

Many estimates indicate that present technologies of the three high-temperature solar systems — linear focus, central receiver, and on-axis concentrators — could produce electricity at a cost that is two to three times larger than that of coal or natural gas plants. The development areas suggested in the Priority Research Directions document should lead to the cost reductions required to make this technology competitive with conventional electricity production within five to ten years, assuming fossil fuels remain at present prices.

Concentrated Solar Thermochemical Processes

Solar thermochemical processes can be used to generate a primary fuel source. The concentrating component of these systems is identical to that of concentrated solar thermal processes for power generation, but the energy conversion is a thermochemical process converting radiation to heat to chemical potential. These systems provide an effective means for long-term storage and transportation of solar energy in the form of fuel and for its utilization in motor vehicles and industrial applications. The basic concept is shown in Figure 77.
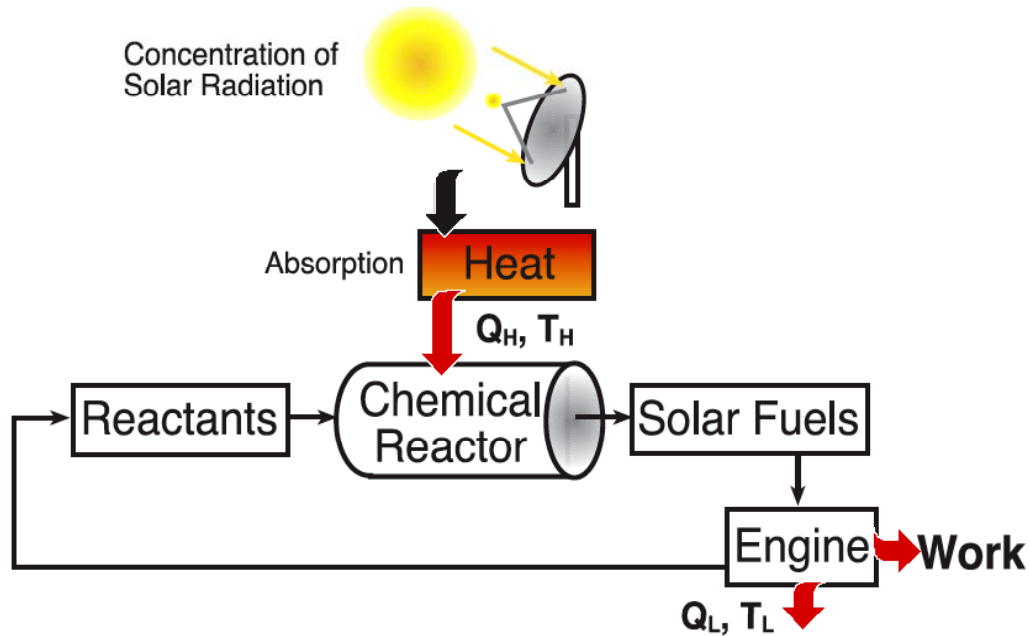
Figure 77 General concept of solar-driven thermochemical cycle

Some examples of solar thermochemical processes are as follows:

Methane reforming:

    (a) $CH_4 + H_2O \rightarrow 3H_2 + CO$

    (b) $CH_4 + CO_2 \rightarrow 2H_2 + 2CO$
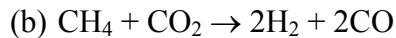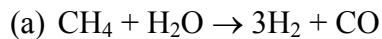
Reaction (a) can be used as fuel enrichment, while (b) can be reversed (i.e., run in a closed loop as shown in Figure 77).

Metal oxide reductions:

    (a) $M_xO_y \rightarrow xM + y/2O_2$

    (b) $M_xO_y + yC \rightarrow xM + yCO$

    (c) $M_xO_y + yCH_4 \rightarrow xM + y(2H_2 + CO)$
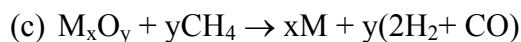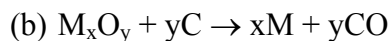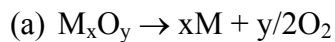
Here M represents a given metal such as zinc, iron, magnesium, or boron. When direct dissociation [reaction (c)] is impractical, the use of carbon or methane can often facilitate the reaction [reactions (d) and (e)].

Water dissociation:

    (a) $H_2O \rightarrow H_2 + 1/2O_2$
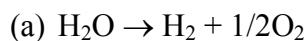
A number of multistep thermal processes and high-temperature electrolysis methods have been developed in an attempt to enable this reaction.

An overview of solar thermochemical processes is provided by Steinfeld and Palumbo (2001). Some of the topics addressed by recent studies are an evaluation of novel processes for fuel synthesis (Möller et al. 2002; Dahl et al. 2004) and material production (Murray et al. 1995; Wieckert et al. 2004); development of novel solar reactors (Anikeev et al. 1998; Osinga et al. 2004); and catalyst development for solar-driven high-temperature gas-gas reactions (Berman and Epstein 1997).

Solar fuel productions will probably be two to three times more expensive than present high-emission industrial methods. However, various studies predict that solar fuels production can be competitive if carbon emission cost is considered.

Concentrated Photovoltaic Systems

Although not strictly a solar thermal process, we discuss here the fast-developing field of concentrated photovoltaic systems — systems that rely on optical configurations similar to those used for concentration in solar thermal processes. In this method, sunlight is concentrated by using mirrors or lenses that are much cheaper than PV panels, and the concentrated light is focused onto the PV cells. The required cell area is therefore reduced by the concentration factor, which in present systems can be as high as 500; future cells may be able to sustain even higher concentration ratios. The higher the concentration is, the smaller is the cell area, and the influence of cell cost on overall system cost is diminished. This approach enables the use of the most efficient PV cells available because when the cell area is very small, the cost reduction due to the increase in cell efficiency outweighs the cost increase associated with high-performance cells. Mature high-concentration PV systems should cost about 40–60% of standard flat PV systems and provide 10–20% more energy than standard PV systems with the same installed power rating.

Some concentrated PV (CPV) systems have one-axis trackers, similar to that shown in Figure 74, and they concentrate the light in one direction, onto a line focus. The concentration ratio of one-axis CPV systems is commonly 10–50. High-concentration PV (HCPV) systems use two-axis trackers and concentrate in two directions; their concentration ratio is typically 200–500. The two-axis HCPV systems are more efficient and less costly.

Recent developments demonstrated the technological feasibility of several CPV and HCPV configurations. These advances include an increase in HCPV cell efficiency (Sherif et al. 2004). Designs of the cell's dense array, used as the power conversion component in some HCPV systems, have been improved (Lasich 2004).

Methods have been developed to provide a uniform high solar flux distribution on the solar cells (Ries et al. 1997b). The performance and durability have been upgraded for Fresnel lenses, which are used as sunlight concentrators in some HCPV systems (Diaz et al. 2004).

Other areas whose development could lead to substantial cost reduction are means to increase the concentration ratio and improve the cooling of the cells. Costs of HCPV systems will continue to drop as the cell efficiency is increased and various other development objectives described in the PRD document are reached. Installed costs of $2–3/W can be reached within five to ten years.

THERMOELECTRICS

Thermoelectric energy conversion technology exploits the thermal energy of electrons for energy conversion between heat and electricity, including power generation, refrigeration, and heat pumping. It is based on the Peltier effect and the Seebeck effect. Because the working fluids are electrons and holes in solids, thermoelectric energy conversion technologies are environmentally benign. A thermoelectric power generator has a maximum efficiency given by

$$\eta = \frac{T_h - T_c}{T_h} \frac{\sqrt{1 + ZT_m} - 1}{\sqrt{1 + ZT_m} + T_c / T_h} \ . \tag{8}$$

A refrigerator has a maximum coefficient of performance (COP) given by

$$COP = \frac{T_c}{T_h - T_c} \frac{\sqrt{1 + ZT_m} - T_h / T_c}{\sqrt{1 + ZT_m} + 1} \ , \tag{9}$$

where

T_h, T_c = temperatures at the hot and cold sides

T_m = mean temperature

Z = thermoelectric figure of merit that is a combination of the Seebeck coefficient S, the electrical conductivity σ, and the thermal conductivity k:

$$Z = \frac{S^2 \sigma}{k}$$

Because Z has a unit of inverse Kelvin, ZT together is called a nondimensional figure of merit.

These expressions show that thermoelectric devices with a high ZT value have an efficiency that approaches the Carnot limit. Thus, the key to thermoelectric technology is finding materials with a large ZT. Because of the conflicting requirements on materials properties, high-ZT materials are elusive. Materials with reasonable ZT are usually heavily doped semiconductors and some semimetals. For making efficient devices, both *n*-type and *p*-type materials with comparable ZT are needed. The ZT values of a material are temperature dependent; they usually peak at certain temperature and drop off at higher temperatures. Thus, refrigeration and power generation often require different materials, depending on the operational temperature range.

The best commercial materials are alloys of Bi_2Te_3 with Bi_2Se_3 (*n*-type) and with Sb_2Te_3 (*p*-type). The alloys are used because phonon thermal conductivity can be reduced significantly with only a small reduction in the electronic power factor ($S^2\sigma$). Bi_2Te_3-based alloys have a maximum ZT around 1 near room temperature. Thus these materials are used for refrigerators. Thermoelectric refrigerators based on these materials have a COP ~ 1 in the same operational temperature range of compressor-based household refrigerators, which have a COP ~3–4. Thus, current commercial materials are not competitive. However, thermoelectric refrigerators have advantages for small refrigeration applications and have found niche markets in a variety of applications, such as picnic coolers, automobile car seats (luxury models), medical equipment, and laser-diode temperature control. Bi_2Te_3-based materials are also used in some power generation applications; however, the module efficiency is limited to 5%. The U.S. National Aeronautics and Space Agency used SiGe alloys (and PbTe-based alloys) to make radioisotope-powered thermoelectric power generators operating in the temperature range of 300–900°C (and 300–600°C for PbTe-based alloys), with a system conversion efficiency ~6–7%. These materials all have a maximum ZT less than but close to 1. Commercial PbTe-based power generation systems using fossil fuel have a fuel-to-electricity efficiency of ~2.5%. The lower efficiency is due to heat loss carried by combustion gas.

The commercial materials discussed above, with a maximum ZT ~ 1, were mostly discovered in the 1950s. Little progress was made in the subsequent years. In the 1990s, the possibility of improving the thermoelectric figure of merit based on electron band-gap engineering and phonon engineering in nanostructures was investigated. These ideas have led to resurgence in thermoelectric research and significant progress in improving ZT, particularly based on nanostructured materials (Chen 2003). Venkatasubramanian et al. (2001) reported that Bi_2Te_3/Sb_2Te_3-based *p*-type superlattices have a room-temperature ZT of 2.4. Harman et al. (2002) reported that PbTe/PbTeSe superlattices with nanodots formed by strain have a room-temperature ZT of 1.6 and a ZT ~ 3.5 around 300°C. Hsu et al. (2004) reported bulk nanostructures of $AgPb_2SbTe_{2+m}$. with a ZT of 2.2 at 527°C. These results suggest that thermoelectric materials can have major impacts in energy conversion technology. Meanwhile, several research projects aiming at improving device efficiency based on more mature materials are underway. The Jet Propulsion Laboratory reported a segmented thermoelectric unicouple with an efficiency of ~14% with the hot side at 975K and cold side at 300K.

Current commercial thermoelectric modules based on Bi2Te3 are at ~\$4.60/W because the market is very small. With current efficiency, it has been projected that the cost can reach \$0.74/W if the annual consumption is more than 2 million modules. If the efficiency can be improved, significant cost reduction is possible. It was projected that \$0.3/W (electrical power) could be realized by using nanostructured materials. Assuming a 35% energy conversion efficiency of thermoelectric devices and a concentrator cost of \$0.24/W (solar input power), the cost of solar-based thermoelectric power generator systems has the potential to reach the \$1–1.5/W (electric) range.

The enabler for the cost/performance improvement is cost-effective materials with high ZT values. Nanostructured materials have broken the ZT ~ 1 barrier, and it seems that ZT ~ 4 is reachable. A major effort should be aimed at mass-producible nanostructures with high ZT and further understanding of the scientific underpinnings of high-ZT values. Other important factors are material reliability, system design, and thermal management.

THERMOPHOTOVOLTAICS

Thermophotovoltaics (TPVs) are similar to solar PVs in that they convert photon energy into electricity. The fundamental difference is that their photon source is a terrestrial heat source rather than the sun. Compared with the sun, a terrestrial heat source has a higher power density and can provide power on rainy days and at night. Thermal radiation from a terrestrial heat source has a longer wavelength, thus, the cells used in a TPV system often have lower band gaps, although silicon-based TPV systems are also of interest. Figure 78 shows the key components of a typical TPV system. A heat source, which can be a fossil fuel combustor, concentrated solar energy, or nuclear reactor, raises the temperature of a solid thermal-radiation emitter to a high temperature, typically to the range of 1,000–1,800°C. Some systems employ filters to reflect photons below the band gap of the PV cells, which are maintained at near room temperature by a thermal management system. The efficiency of a TPV power generator system can be split into several factors:

$$\eta = \eta_{source}\eta_{spectral}\eta_{diode}\eta_{mech} , \qquad\qquad (10)$$

where

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

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

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

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

The TPV diode efficiency has reached 27% (Brown et al. 2003). However, the system efficiency has been relatively low. A combustion-based TPV system has a maximum efficiency of 4.5% because much of the heat carried by the combustion product below the emitter temperature is wasted. As the emitters operate at high temperatures, recuperation of the thermal energy of the combustion products with temperature below the emitter temperatures is essential in improving the system efficiency.

Current consensus among researchers is that TPVs are best suited for cogeneration systems, where solar PV provides energy during sunny days while at night and on rainy days, TPVs provide energy from decentralized home heating systems or energy-intensive industrial systems where high temperatures are available. For example, it has been projected that an installed 1.5-kW home furnace generator costs $4,200 ($2,700 for the furnace and $1,500 for the generator) (Fraas and McConnell 2002). The estimated payback time is four years for a home
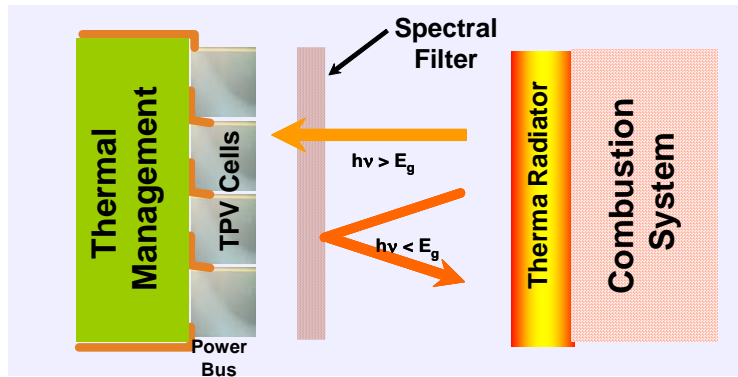
Figure 78 A typical thermophotovoltaic system

furnace TPV cogeneration system at 10 cents per kilowatt-hour. Such a system will reduce the battery dependence of a pure solar system. For a GaSb-based TPV system, the estimated cell cost accounts for 35% of the system cost.

The enablers for the cost and performance improvements are high-temperature selective emitters, lost-cost filters, and efficient system design to recuperate waste heat below the emitter temperature. Selective emitters that are durable for high-temperature operation and yet cost effective, as well as cost-effective spectral filters are essential for system efficiency. Examples of these structures are interference filters, photonic crystal emitters, and rare-earth-doped selective emitters. Although the diodes themselves have impressive efficiency, there is room for further improvements, for example, through band gap engineering, that are widely used in semiconductor lasers and detectors. New concepts such as tunneling and surface-wave-based TPVs (DiMatteo et al. 2001) and coherent thermal emission (Greffet et al. 2002) are worthy of further exploration.

Solar PVs, TPVs, and thermoelectrics cover heat sources of different temperature range and could work together to provide efficient power supplies for distributed systems. TPV diodes evolved from tandem cells used for high-efficiency solar cells. Because thermoelectrics can generate power at a lower temperature range, combined TPV and thermoelectric power generation systems could lead to higher system efficiency.

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APPENDIX 2: WORKSHOP PARTICIPANTS

Workshop for Basic Research Needs for Solar Energy Utilization

Bethesda North Marriott Hotel and Conference Center
Bethesda, Maryland
April 18–21, 2005

Workshop Chair

Nathan S. Lewis, California Institute of Technology

Workshop Co-chair

George Crabtree, Argonne National Laboratory

Panel Chairs

Paul Alivisatos, Lawrence Berkeley National Laboratory
Arthur J. Nozik, National Renewable Energy Laboratory
Michael Wasielewski, Northwestern University

Pre-workshop Briefing Presenter

Jeffrey Mazer, Solar Energy Technologies, U.S. Department of Energy

Plenary Session Speakers

Tom Feist, GE Global Research
Martin Hoffert, New York University
Jeffrey Mazer, Solar Energy Technologies, U.S. Department of Energy

Sub-panel Chairs

Harry Atwater, California Institute of Technology
Allen Bard, University of Texas at Austin
Roberto Car, Princeton University
Gang Chen, Massachusetts Institute of Technology
Carol Creutz, Brookhaven National Laboratory
Graham Fleming, Lawrence Berkeley National Laboratory
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Rienk van Grondelle, Vrije University, Netherlands
Rama Venkatasubramanian, RTI International
Wladek Walukiewicz, Lawrence Berkeley National Laboratory
Michael Wasielewski, Northwestern University
Paul Weiss, Pennsylvania State University
Frank Willig, Hahn-Meitner Institute, Germany
Jerry Woodall, Purdue University
Peter Würfel, University of Karlsruhe, Germany
Shozo Yanagida, Osaka University
Peidong Yang, Lawrence Berkeley National Laboratory
Alex Zunger, National Renewable Energy Laboratory

APPENDIX 3: WORKSHOP PROGRAM

Workshop for Basic Research Needs for
Solar Energy Utilization

**Bethesda North Marriott Hotel and Conference Center
Bethesda, Maryland
April 18–21, 2005**

Agenda for Plenary Sessions

Plenary Opening Session — Monday, April 18, 2005

Time	Topic	Speaker or Location
7:30 – 8:30 a.m.	Registration and Continental Breakfast	Salon E
8:30 – 8:35 a.m.	Welcome and Workshop Charter	Pat Dehmer, Director, Office of Basic Energy Sciences
8:35 – 8:55 a.m.	A Global Perspective on the Role of Solar Energy as a Primary Energy Source	Nathan Lewis, Workshop Chair, California Institute of Technology, and George Crabtree, Workshop Co-chair, Argonne National Laboratory
8:55 – 9:25 a.m.	Overview of DOE/EERE Solar Energy Technologies Program, Related EERE Efforts, and Basic Research Needs	Jeff Mazer, DOE Energy Efficiency and Renewable Energy
9:25 – 9:55 a.m.	Solar-Renewable Energy for a Greenhouse Planet	Martin Hoffert, Professor, Physics Dept., New York University
9:55 – 10:25 a.m.	An Industrial Perspective on the Opportunities and Challenges Involved with the Widespread Use of Solar Energy in Global Power Production	Tom Feist, GE Global Research
10:25 – 10:45 a.m.	Break	Salon E
10:45 – 11:10 a.m.	Solar Electricity Panel Overview	Arthur Nozik, Senior Research Fellow, National Renewable Energy Laboratory
11:10 – 11:35 a.m.	Solar Fuels Panel Overview	Michael Wasielewski, Professor, Chemistry Dept., Northwestern University
11:35 a.m. – 12 noon	Cross-cutting Panel Overview	Paul Alivisatos, Director, Materials Science Division, Lawrence Berkeley National Laboratory
12:00 – 12:15 p.m.	Closing Remarks for Opening Plenary Session	Nathan Lewis, Workshop Chair, California Institute of Technology
12:15 – 1:30 p.m.	Lunch	Salon D

Plenary Closing Session — Wednesday Afternoon, April 20, 2005

Time	Topic	Speaker or Location
1:00 – 1:15 p.m.	Opening Remarks for Workshop Report Out	George Crabtree, Workshop Co-chair, Argonne National Laboratory
1:15 – 2:05 p.m.	Solar Electric Panel Survey and Priority Research Directions Presentation	Solar Electric Panel
2:05 – 3:00 p.m.	Solar Fuels Panel Survey and Priority Research Directions Presentation	Solar Fuels Panel
3:00 – 3:20 p.m.	Break	Salon E
3:20 – 4:30 p.m.	Cross-cutting Panel Survey and Priority Research and Cross-cutting Research Directions Presentation	Cross-cutting Panel
4:30 – 4:50 p.m.	Workshop Concluding Remarks	Nathan Lewis, Workshop Chair, California Institute of Technology, and George Crabtree, Workshop Co-chair, Argonne National Laboratory
4:50 – 5:00 p.m.	Final Closing Remarks	Pat Dehmer, Director, Office of Basic Energy Sciences
5:00 – 6:00 p.m.	Reception (All)	Glen Echo Foyer Area
6:00 p.m.	Workshop Adjourns	

Agenda for Solar Electric Breakout Sessions
Panel Chair: A.J. Nozik

Monday, April 18, 2005, 1:30 p.m. – 9:00 p.m.

Panel 1A (Inorganic PV) — Glen Echo Room

Time	Topic	Speaker or Location
Session 1		
1:30 – 1:45 p.m.		Sub-panel Co-chairs, H. Atwater and A.J. Nozik
1:45 – 2:15 p.m.	Thermodynamic Limits and Approaches to 3rd Generation Photovoltaics (PVs)	Peter Würfel
2:15 – 2:45 p.m.	New Concepts in Photovoltaics for Widespread Use	Antonio Luque
2:45 – 3:15 p.m.	Nanocrystals and Solar Photon Conversion	Louis Brus
3:15 – 3:45 p.m.	Basic Research Needs for Very-high-efficiency III-V Multijunction Cells	Richard King
3:45 – 4:00 p.m.	Coffee Break	
4:00 – 5:45 p.m.	Initial Discussion of one-sentence Priority Research Directions (PRDs)	
6:00 – 7:30 p.m.	Working Dinner	Salon D
Session 2		
7:30 – 9:00 p.m.	Prioritize 3–5 one-sentence PRDs	
9:00 – 9:30 p.m.	Panel Chair and Sub-panel Co-chairs review PRDs	Salon A

Panel 1B (Organic PV) — Forest Glen Room

Time	Topic	Speaker or Location
Session 1		
1:30 – 1:45 p.m.		Sub-panel Co-chairs, A.J. Heeger and G. Rumbles
1:45 – 2:15 p.m.	Small Molecular Weight Organic Solar Cells: Concepts and Results	Steve Forrest
2:15 – 2:45 p.m.	Excitonic Solar Cells	Brian Gregg
2:45 – 3:15 p.m.	Fundamental Processes of Charge Injection, Transport, and Charge Separation in Organic Materials	Daryl Smith
3:15 – 3:45 p.m.	Polymer and Hybrid Solar Cells: Status and Challenges	Rene A.J. Janssen
3:45 – 4:00 p.m.	Coffee Break	
4:00 – 5:45 p.m.	Initial Discussion of one-sentence PRDs	
6:00 – 7:30 p.m.	Working Dinner	Salon D
Session 2		
7:30 – 9:00 p.m.	Prioritize 3–5 one-sentence PRDs	
9:00 – 9:30 p.m.	Panel Chair and Sub-panel Co-chairs review PRDs	Salon A

Panel 1C (Photoelectrochemistry) — Brookside A Room

Time	Topic	Speaker or Location
Session 1		
1:30 – 1:45 p.m.		Sub-panel Co-chairs, A.J. Bard and B.A. Parkinson
1:45 – 2:15 p.m.	The Past, Present, and Future of Photoelectrochemistry	Mary Archer
2:15 – 2:45 p.m.	Mesoscopic Injection Solar Cells	Michael Grätzel
2:45 – 3:15 p.m.	Photoelectrolysis	Bruce Parkinson
3:15 – 3:45 p.m.	Industrial Aspects of Photoelectrochemical Energy Conversion	Keith Brooks
3:45 – 4:00 p.m.	Coffee Break	
4:00 – 5:45 p.m.	Initial Discussion of one-sentence PRDs	
6:00 – 7:30 p.m.	Working Dinner	Salon D
Session 2		
7:30 – 9:00 p.m.	Prioritize 3–5 one-sentence PRDs	
9:00 – 9:30 p.m.	Panel Chair and Sub-panel Co-chairs review PRDs	Salon A

Tuesday, April 19, 2005, 8:00 a.m. – 9:30 p.m.

Panels 1A, 1B, and 1C

Time	Topic	Speaker or Location
Session 3 (separate sessions)		
8:00 – 10:00 a.m.	Draft 3–5 one-sentence and one-viewgraph PRDs for each Sub-panel	Panel 1A — Glen Echo Room Panel 1B — Forest Glen Room Panel 1C — Brookside A Room
10:00 – 10:15 a.m.	Coffee Break	
10:15 a.m. – 12:30 p.m.	Plenary Midpoint Session (Presentations of Draft PRDs)	Salon E
12:30 – 1:30 p.m.	Working Lunch	Salon D
Session 4 (unified sessions)		
1:30 – 6:00 p.m.	Down-select to 7–9 PRDs for Panel 1	Salon A
Session 5 (unified sessions)		
7:30 – 9:30 p.m.	Open time for further discussion sessions if needed	Salon A

Wednesday, April 20, 2005, 8:00 a.m. – 5:00 p.m.

Panels 1A, 1B, and 1C

Time	Topic	Speaker or Location
Session 6		
8:00 am – 12:00 noon	Draft four-viewgraph Panel Survey Draft one Executive Summary paragraph, one viewgraph, and a 1,000–1,500 word version of each PRD Begin drafting 3,000–5,000 word Panel Surveys	Salon A
12:00 – 1:00 p.m.	Working Lunch	Salon D
1:00 – 5:00 p.m.	Closing Plenary Session	Salon E
5:00 – 6:00 p.m.	Reception	Glen Echo Foyer

Thursday, April 21, 2005, 8:00 a.m. – 3:30 p.m.

Final Writing of Panel Report — Writers and Co-chairs Only

Time	Topic	Speaker or Location
8:00 am – 3:30 p.m.	Selected writers, panel chairs, and co-chairs complete writing and integration of Panel Surveys, PRDs, CCRDs, and Factual Documents into final Workshop Report	Forest Glen Room

Agenda for Solar Fuels Breakout Sessions
Panel Chair: M.R. Wasielewski

Monday, April 18, 2005, 1:30 p.m. – 9:00 p.m.

Panel 2A (Bioinspired Assemblies for Photochemical Energy Conversion) — Salon F

Time	Topic	Speaker or Location
Session 1		
1:30 – 1:45 p.m.		Sub-panel Co-chairs, M.R. Wasielewski and D. Gust
1:45 – 2:15 p.m.	To be announced	Thomas Moore
2:15 – 2:45 p.m.	Light-Collecting Supramolecular Assemblies based on Coordination Chemistry	Joseph Hupp
2:45 – 3:15 p.m.	Beyond the Single Electron: Coupled Electron Transfers in Artificial Photosynthesis	Leif Hammarstrom
3:15 – 3:45 p.m.	Realizing Long-lived Charge Separation in Artificial Photosynthetic Systems	Anthony Harriman
3:45 – 4:00 p.m.	Coffee Break	
4:00 – 5:45 p.m.	Initial Discussion of one-sentence Priority Research Directions (PRDs)	
6:00 – 7:30 p.m.	Working Dinner	Salon D
Session 2		
7:30 – 9:00 p.m.	Prioritize 3–5 one-sentence PRDs	
9:00 – 9:30 p.m.	Panel Chair and Sub-panel Co-chairs review PRDs	Salon B

Panel 2B (Natural Photosynthetic Systems) — Brookside B Room

Time	Topic	Speaker or Location
Session 1		
1:30 – 1:45 p.m.		Sub-panel Co-chairs, G.R. Fleming and J.R. Norris
1:45 – 2:15 p.m.	To be announced	Richard Cogdell
2:15 – 2:45 p.m.	Light-harvesting and Charge Separation in Photosystem II	Rienk vanGrondelle
2:45 – 3:15 p.m.	Protein Design for Stabilization of Electron and Proton Transfer Reactions	Marilyn Gunner
3:15 – 3:45 p.m.	The Oxygen-evolving Complex of Photosystem II	Gary Brudvig
3:45 – 4:00 p.m.	Coffee Break	
4:00 – 5:45 p.m.	Initial Discussion of one-sentence PRDs	
6:00 – 7:30 p.m.	Working Dinner	Salon D
Session 2		
7:30 – 9:00 p.m.	Prioritize 3–5 one-sentence PRDs	
9:00 – 9:30 p.m.	Panel Chair and Sub-panel Co-chairs review PRDs	Salon B

Panel 2C (Photocatalytic Cycles and Photodriven Chemical Reactions) — Seneca Boardroom

Time	Topic	Speaker or Location
Session 1		
1:30 – 1:45 p.m.		Sub-panel Co-chairs, C. Creutz and D. Nocera
1:45 – 2:15 p.m.	Water-splitting to Form Hydrogen and Oxygen	Thomas Mallouk
2:15 – 2:45 p.m.	Proton-coupled Electron Transfer/Multiple Electron Transfer	Thomas Meyer
2:45 – 3:15 p.m.	Collecting Multiple Electrons into a Single Subunit of a Multicomponent Species	Sebastiano Campagna
3:15 – 3:45 p.m.	Molecular Chemistry of Renewable Energy	Daniel Nocera
3:45 – 4:00 p.m.	Coffee Break	
4:00 – 5:45 p.m.	Initial Discussion of one-sentence PRDs	
6:00 – 7:30 p.m.	Working Dinner	Salon D
Session 2		
7:30 – 9:00 p.m.	Prioritize 3–5 one-sentence PRDs	
9:00 – 9:30 p.m.	Panel Chair and Sub-panel Co-chairs review PRDs	Salon B

Panel 2D (Biofuels) — Oakley Room

Time	Topic	Speaker or Location
Session 1		
1:30 – 1:45 p.m.		Sub-panel Co-chairs, Chris Somerville and Bob Tabita
1:45 – 2:15 p.m.	Advantages and Disadvantages of the Nitrogenase/Hydrogenase System for Biohydrogen Production	Paul Ludden
2:15 – 2:45 p.m.	Biological Methane Production	John Reeve
2:45 – 3:15 p.m.	Direct Biohydrogen Production from Oxygenic Photosynthetic Microorganisms	Mike Seibert
3:15 – 3:45 p.m.	Biomass to Ethanol: State of the Art	Mike Himmel
3:45 – 4:00 p.m.	Coffee Break	
4:00 – 5:45 p.m.	Initial Discussion of one-sentence PRDs	
6:00 – 7:30 p.m.	Working Dinner	Salon D
Session 2		
7:30 – 9:00 p.m.	Prioritize 3–5 one-sentence PRDs	
9:00 – 9:30 p.m.	Panel Chair and Sub-panel Co-chairs review PRDs	Salon B

Tuesday, April 19, 2005, 8:00 a.m. – 9:30 p.m.

Panels 2A, 2B, 2C, and 2D

Time	Topic	Speaker or Location
Session 3 (separate sessions)		
8:00 – 10:00 a.m.	Draft 3–5 one-sentence and one-viewgraph PRDs for each Sub-panel	Panel 2A — Salon F Panel 2B — Brookside B Room Panel 2C — Seneca Boardroom Panel 2D — Oakley Room
10:00 – 10:15 a.m.	Coffee Break	
10:15 a.m. – 12:30 p.m.	Plenary Midpoint Session (Presentations of draft PRDs)	Salon E
12:30 – 1:30 p.m.	Working Lunch	Salon D
Session 4 (unified sessions)		
1:30 – 6:00 p.m.	Down-select 7–9 PRDs for Panel 1	Salon F
Session 5 (unified sessions)		
7:30 – 9:30 p.m.	Open time for further discussion sessions if needed	Salon F

Wednesday, April 20, 2005, 8:00 a.m. – 5:00 p.m.

Panels 2A, 2B, 2C, and 2D

Time	Topic	Speaker or Location
Session 6		
8:00 a.m. – 12:00 noon	Draft four-viewgraph Panel Survey Draft one Executive Summary paragraph, one viewgraph, and a 1,000–1,500 word version of each PRD Begin drafting 3,000–5,000 word Panel Surveys	Salon B
12:00 – 1:00 p.m.	Working Lunch	Salon D
1:00 – 5:00 p.m.	Closing Plenary Session	Salon E
5:00 – 6:00 p.m.	Reception	Glen Echo Foyer

Thursday, April 21, 2005, 8:00 a.m. – 3:30 p.m.

Final Writing of Panel Report — Writers and Co-chairs Only

Time	Topic	Speaker or Location
8:00 am – 3:30 p.m.	Selected writers, panel chairs, and co-chairs complete writing and integration of Panel Surveys, PRDs, CCRDs, and Factual Documents into final Workshop Report	Glen Echo Room

Agenda for Cross-cutting Breakout Sessions
Panel Chair: P. Alivisatos

Monday, April 18, 2005, 1:30 p.m. – 9:00 p.m.

Sub-panel 3A — Linden Oak Room

Time	Topic	Speaker or Location
Session 1		
1:30 – 1:45 p.m.		Sub-panel Co-chairs, Jacob Karni and Gang Chen
1:45 – 1:55 p.m.	Solar Hot Water Systems	Jane Davidson
1:55 – 2:05 p.m.	Concentrated Solar Thermal Processes for Power Generation	Robert Pitz-Paal
2:05 – 2:15 p.m.	Concentrated Solar Thermochemical Processes	Aldo Steinfeld
2:15 – 2:25 p.m.	Concentrated Photovoltaics	Herb Hayden
2:25 – 3:00 p.m.	Discussion of Concentration Processes	
3:00 – 3:30 p.m.	New Materials for Direct Heat to Electric Energy Conversion — the Thermoelectric Option	Mercouri G. Kanatzidis
3:30 – 4:00 p.m.	Current Status of Thermophotovoltaic Generation of Electricity	Andreas Gombert
4:00 – 4:15 p.m.	Coffee Break	
4:15 – 5:15 p.m.	Initial discussion of one-sentence Priority Research Directions (PRDs)	
6:00 – 7:30 p.m.	Working Dinner	Salon D
Session 2		
7:30 – 9:00 p.m.	Prioritize 3–5 one-sentence PRDs	
9:00 – 9:30 p.m.	Panel Chair and Sub-panel Co-chairs review PRDs	

Tuesday, April 19, 2005, 8:00 a.m. – 9:30 p.m.

Time	Topic	Speaker or Location
Session 3		
8:00 – 10:00 a.m.	Draft 3–5 one-sentence and one-viewgraph PRDs	Linden Oak Room
10:00 – 10:15 a.m.	Coffee Break	
10:15 a.m. – 12:30 p.m.	Plenary Midpoint Session (Presentations of draft PRDs)	Salon E
12:30 – 1:30 p.m.	Working Lunch	Salon D
Session 4		
1:30 – 6:00 p.m.	Down-select 3–4 PRDs	Glen Echo Room
Session 5		
7:30 – 9:30 p.m.	Open time for further discussion sessions if needed	Glen Echo Room

Wednesday, April 20, 2005, 8:00 a.m. –5:00 p.m.

Time	Topic	Speaker or Location
Session 6		
8:00 a.m. – 12:00 noon	Draft four-viewgraph Panel Survey Draft one Executive Summary paragraph, one viewgraph, and a 1,000–1,500 word version of each PRD Begin drafting 3,000–5,000 word Panel Surveys	Glen Echo Room
12:00 – 1:00 p.m.	Working Lunch	Salon D
1:00 – 5:00 p.m.	Closing Plenary Session	Salon E
5:00 – 6:00 p.m.	Reception	Glen Echo Foyer

Thursday, April 21, 2005, 8:00 a.m. – 3:30 p.m.

Final Writing of Panel Report — Writers and Co-chairs Only

Time	Topic	Speaker or Location
8:00 a.m. – 3:30 p.m.	Selected writers, panel chairs, and co-chairs complete writing and integration of Panel Surveys, PRDs, CCRDs, and Factual Documents into final Workshop Report	Linden Oak Room

Agenda for Cross-cutting Breakout Sessions
Panel Chair: P. Alivisatos

Monday, April 18, 2005, 1:30 p.m. – 9:00 p.m.

Sub-panels 3B, 3C, and 3D

Time	Topic	Speaker or Location
Lunch	Panels 3B, 3C, 3D meet at sub-panel-reserved tables to discuss activities pending for Tuesday and Wednesday	Salon D
Session 1		
1:30 – 5:00 p.m.	Roam to Panels 1, 2, 3A. Please see their agendas on web or in your information folder for speaker lists and PRD discussions.	
6:00 – 7:30 p.m.	Working Dinner	Salon D
Session 2		
7:30 – 9:00 p.m.	Roam: join panels 1, 2, 3A as they each prioritize 3–5 one-sentence PRDs	
9:00 – 9:30 p.m.	Panels 1 and 2: Panel chair and Sub-panel Co-chairs only, to review PRDs	

Tuesday, April 19, 2005, 8:00 a.m. – 9:30 p.m.

Time	Topic	Speaker or Location
Session 3		
8:00 – 10:00 a.m.	Roam: join panels 1, 2, 3A as they draft one-sentence, one-viewgraph PRDs	
10:00 - 10:15 a.m.	Coffee Break	
10:15 a.m. – 12:30 p.m.	Plenary midpoint session: join other panels as they present PRDs to entire workshop	
12:30 – 1:30 p.m.	Working Lunch	Salon D
Session 4		
1:30 – 6:00 p.m.	Breakout sessions for Panels 3B, C, D; formulate 5–7 one-sentence CCRDs per Sub-panel; down-select for 2–3 CCRDs per Sub-panel, and begin drafting one-paragraph versions of CCRDs	Sub-panel 3B — Brookside A Sub-panel 3C — Brookside B Sub-panel 3D — Forest Glen
Session 5		
7:30 – 9:30 p.m.	Continue development of CCRDs, 2–3 per Sub-panel: one paragraph, one viewgraph; begin to draft full CCRDs of 750 words each	Sub-panel 3B — Brookside A Sub-panel 3C — Brookside B Sub-panel 3D — Forest Glen

Wednesday, April 20, 2005, 8:00 a.m. – 5:00 p.m.

Time	Topic	Speaker or Location
Session 6		
8:00 a.m. – 12:00 noon	Breakout Session for all Sub-panels: Panels 3B,C,D finish one-paragraph, one-viewgraph CCRDs, draft four-viewgraph panel surveys, continue to draft CCRDs and the introduction to CCRDs	Sub-panel 3B — Linden Oak Sub-panel 3C — Salon B Sub-panel 3D — Forest Glen
12:00 – 1:00 p.m.	Working Lunch	Salon D
1:00 – 5:00 p.m.	Closing Plenary Session	
5:00 – 6:00 p.m.	Reception	Glen Echo Foyer

Thursday, April 21, 2005, 8:00 a.m. – 3:30 p.m.

Final Writing of Panel Report — Writers and Co-chairs Only

Time	Topic	Speaker or Location
8:00 a.m. – 3:30 p.m.	Selected writers, panel chairs, and co-chairs complete writing and integration of Panel Surveys, PRDs, CCRDs, and Factual Documents into final Workshop Report	Linden Oak Room

APPENDIX 4: ADDITIONAL READING

ADDITIONAL READING

D.M. Adams, L. Brus, C.E.D. Chidsey, S. Creager, C. Creutz, C.R. Kagan, P.V. Kamat, M. Lieberman, S. Lindsay, R.A. Marcus, R.M. Metzger, M.E. Michel-Beyerle, J.R. Miller, M.D. Newton, D.R. Rolison, O. Sankey, K.S. Schanze, J. Yardley, and X.Y. Zhu, "Charge Transfer on the Nanoscale: Current Status," *J. Phys. Chem. B* **107**(28), 6668–6697 (July 17, 2003).

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INDEX

INDEX