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RESEARCH OPPORTUNITIES IN PHOTOCHEMICAL SCIENCES

WORKSHOP PROCEEDINGS

FEBRUARY 5-8, 1996
ESTES PARK, COLORADO

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Acknowledgments

First, we wish to acknowledge and sincerely thank all the Plenary Speakers, the NREL Program Managers who presented overviews on U.S. Department of Energy energy technology programs, the Panel chairs, and the Panel members who participated in this workshop and made this report possible; they are all listed in Appendix A. We also thank Drs. Robert Marianelli and Allan Laufer of the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research for their support and encouragement. Finally, we are deeply indebted to Kim Prinzi Kimbro for her invaluable help in coordinating all aspects of the workshop logistics and report production, as well as Jill Harty, and Cricket Pierce of the NREL Conferences group for their work in helping to organize the workshop. We thank Dr. Harry Dewey for his help in putting the workshop report on the Web.

Arthur J. Nozik
Silvia Ronco

Executive Summary

The workshop entitled "*Research Opportunities in Photochemical Sciences*" was initiated by the U.S. Department of Energy (DOE), Office of Energy Research (ER), Office of Basic Energy Sciences (BES), Division of Chemical Sciences. The National Renewable Energy Laboratory (NREL) in Golden, Colorado was requested by ER to host the workshop. It was held February 5-8, 1996 at the Estes Park Conference Center, Estes Park, CO, and attended by about 115 leading scientists and engineers from the U.S., Japan, and Europe; program managers for the DOE ER and Energy Efficiency and Renewable Energy (EERE) programs also attended.

The purpose of the workshop was to bridge the communication gap between the practioneers and supporters of basic research in photochemical science and the practioneers and supporters of applied research and development in technologies related to photochemical science. For the purposes of the workshop the definition of the term "photochemical science" was broadened to include homogeneous photochemistry, heterogeneous photochemistry, photoelectrochemistry, photocatalysis, photobiology (for example, the light-driven processes of biological photosynthesis and proton pumping), artificial photosynthesis, solid state photochemistry, and solar photochemistry. The technologies under development through DOE support that are most closely related to photochemical science, as defined above, are the renewable energy technologies of photovoltaics, biofuels, hydrogen energy, carbon dioxide reduction and utilization, and photocatalysis for environmental cleanup of water and air. An important objective was to identify and define the photochemical science that underpins and is critical for the ultimate successful development of the EERE technologies just described. The workshop was to provide a forum to discuss and highlight the current state of photochemical science, and to show the importance and relevance of photochemical science to both existing and potential future energy technologies.

The first set of presentations at the workshop were four 20-min overview talks by EERE/NREL program managers on their programs in photovoltaics, biofuels, hydrogen, and photocatalysis. These four talks were then followed by a series of 9 Plenary Talks that defined and summarized photochemical science in the areas of photochemical dye sensitization at semiconductor-liquid interfaces, organic photovoltaic systems, solid state photochemistry in amorphous silicon, molecular prescursors for electronic and photovoltaic materials, solar hydrogen production, homogeneous and heterogeneous photocatalysis, basic mechanisms of photosynthesis, and artificial photosynthesis. The workshop then broke up into six panels to discuss, in detail, the science and its present and future impact on technology; each panel member made a presentation on their work and perspective. The panels then met in a Plenary session to report the results of their initial discussions, and to obtain input from the all the workshop participants. Final panel reports were then prepared during further group discussions.

The topics of the six panels were: A-1: Photochemical and Organic-Based Solar Cells; A-2: Solid State Photochemistry; B-1: Photochemical Reduction of CO_2 to Fuels and Chemicals; B-2: Solar Hydrogen Production; B-3: Photodetoxification and Purification of Water and Air; and C-1 Basic Mechanisms of Photosynthesis and Conversion of Biomass to Fuels and Chemical Products.

For panel A-1, the major challenges that were identified were to (1) improve the stability of photoelectrochemical and photochemical solar cells, (2) improve their efficiency , (3) discover new inorganic and organic semiconducting materials and sensitizers; and (4) discover new electrocatalysts compatible with the semiconductor electrodes. This will require balanced research programs on fundamental mechanisms of inorganic and organic semiconductor electrode corrosion and passivation, dye sensitization processes, development of improved theoretical models of heterogeneous electron and hole transfer across inorganic and organic semiconductor interfaces with liquids and metals, new techniques to measure electron transfer kinetics, new organic and inorganic electrode and catalyst materials, and the chemistry of semiconductor surfaces and interfaces in contact with redox electrolytes and other phases.

In panel A-2, the identified challenges related to the solid state chemistry of amorphous silicon include understanding the role of hydrogen, the properties and microstructure of amorphous and microcrystalline Si alloys, the kinetics of defect creation and annealing, photoinduced metastability, and the detailed nature of interfaces with amorphous Si. Recommended research areas included growth and characterization of amorphous Si with low hydrogen content; study of passivants or bond terminators other than hydrogen; study of the interaction of light and the effects of light on defects, dopants, and hydrogen; the relationship between light-enhanced hydrogen motion, metastability, and photoinduced structural changes; studies of light-induced effects in amorphous hydrogenated germanium; the effects of alloying, voids, clusters, and strain; study of energy dissipation mechanisms, studies of the photochemistry of defect generation and annealing, and theoretical understanding of local bonding, defect generation, and annealing. In the area of molecular precursors for electronic materials the stated challenges and opportunities are phase and composition control, dopant atom location and concentration, ordered nanostructures, interfacial control, mechanisms of materials growth and processing, and alternative deposition strategies.

For photochemical reduction of CO_2, panel B-1 recommended research to develop efficient and stable photosensitizers and photocatalysts, studies of the photophysics and photochemistry of molecular excited states, further understanding of photoinduced electron and hole transfer and separation, development of thermal, electro- and photo-catalysts with high activity and low thermodynamic overpotentials, and detailed mechanistic and kinetic studies.

In panel B-2 on solar hydrogen production, the challenges and research opportunities were identified as developing improved photocatalysts (homogeneous and heterogeneous) for water splitting, extension of the activity of photocatalysts capable of splitting water into the visible region of the solar spectrum, control of the energetics of the water splitting redox chemistry to match the available energetics of the photocatalyst, improvement of the long term photostability of the solar water splitting system, investigation of microheterogeneous systems that combine molecular and solid state components, and novel schemes for collecting, storing, and releasing hydrogen as needed for applications.

In the B-3 panel on photodetoxification and purification of air and water, the challenges and opportunities were identified as better modeling and understanding of the involved chemical

reactions and intermediates, innovation in reactor design, scale-up studies for photochemical reactors, the discovery and development of more efficient photocatalysts for both water and air cleanup, extension of the photoactivity into the visible region of the solar spectrum, and integration of the photochemistry with other biological and physical approaches.

Finally, the panel on photosynthesis and conversion of biomass to fuels and chemical identified the following critical research opportunities: better understanding of the fundamental principles of photoinduced energy and charge transfer in natural and artificial photosystems as functions of structure, energetics, and medium; expansion of the repertoire of donors and acceptors that optimize the fraction of captured photon energy; better understanding of the effect of the intervening medium between the donor and the acceptor on the electronic coupling; determination of the structures of transient intermediates; fundamental understanding of the physics and chemistry of single photosystem photosynthesis (and its mimetic analogs), and the coupling of simple stand-alone biological photosystems, such as Photosystem II, purple and green bacteria, as well as halobacteria, to fuel forming reactions; deeper understanding of the diverse mechanisms involved in the antenna function in natural and artificial photosynthesis; investigation of charge separation molecules that are fully functional in rigid media and in confined environments; studies of the mechanisms of assembly of natural and artificial supramolecular light-utilizing systems, and the design and construction of hybrid systems using donor-acceptor systems along with synthetic peptides, polymers, nanocrystallites, and electrode surfaces; studies of the nature of the interaction of molecular and supramolecular assemblies with their surroundings; exploration of (a) the role of solvent dynamics on charge separation reactions and (b) electron donor-acceptor systems and their photochemistry in anisotropic media e.g., liquid crystals, and pulled and/or stretched polymers; design of multi-redox charge accumulators, analogous to the Oxygen Evolving Complex of Photosystem II; exploration of the coupling of proton movement to charge transfer; better understanding of the mechanisms of regulation, protection, and repair of artificial and natural photosynthetic systems; studies of energy efficient supramolecular systems; exploration of artificial photosynthetic molecules that use two sequential one-photon events within the same molecular system; and studies of the dark reactions necessary for long term-storage and utilization of solar energy, as well as, studies of the catalytic activity of the agents that promote the secondary reactions.

Detailed descriptions and discussions of all these research opportunities and challenges are presented in the individual panel reports.

Arthur J. Nozik

Workshop Objectives and Plan

DOE/BES Workshop
February 5-8, 1996
Estes Park, CO

RESEARCH OPPORTUNITIES IN PHOTOCHEMICAL SCIENCES

Objectives

- Bridge communication gap between basic research in photochemistry and applied research and development in relevant energy technologies (e.g., photovoltaics, biofuels, hydrogen, photodetoxification, and future energy technologies such as solar photoconversion)
- Define and elaborate the science that's relevant to energy technology
  - ♦ Evaluate its present status regarding the level of basic understanding.
  - ♦ Understand the barriers to implementation of current energy technologies.
  - ♦ Explain how the science can impact or lead to elimination of these barriers.
  - ♦ Connect the science to potential new energy technologies that are not yet under development.
  - ♦ Define new areas of photochemical science that will be of intrinsic scientific importance and also of potential significance for energy technology.
- For the specific case of photochemical science and energy technology--demonstrate unequivocally how basic research underpins and provides a critical intellectual foundation for technology development.

Workshop Schedule

Research Opportunities in Photochemical Sciences
Estes Park, Colorado
February 5 - 8, 1996

Monday, February 5		
7:30 - 9:30 p.m. Library)	Welcoming Reception and Registration (Conf. Center-Foyer	
Tuesday, February 6		
7:00 - 8:00 a.m.	Breakfast (Salon E and F)	
7:30 - 8:00	Registration	
8:00 - 8:30	Welcome and Introduction	A.J. Nozik, Workshop Chair; S. Ronco, DOE/BES; B. Marshall, NREL Deputy Director for Operations
8:30 - 8:45	Report on DOE/ER/Chem. Sci. Programs	A. Laufer, DOE/BES
8:45 - 9:45	Reports on DOE/EE Programs (15 min. ea.) Photovoltaics, J. Benner (NREL) Biofuels, J. Mielenz (NREL) Hydrogen, C. Gregoire Padro (NREL) Photodetoxification, C. Lyons (NREL)	
9:45 - 2:45	PLENARY TALKS Chair: Silvia Ronco	
9:45 - 10:10	Talk A-1:	M. Grätzel, "*Light Energy Harvesting and Conversion by Mesoporous Thin Film Devices*"
10:10 - 10:30	Coffee Break	
10:30 - 10:45	Talk A-1 (#2)	G. Bird, "*Organic Semiconductors*"
10:45 - 11:10	Talk A-2:	H. Fritzsche, "*Light-Induced Metastable Structural Changes in Amorphous Semiconductors*"
11:10 - 11:25	Talk A-2 (#2)	W. Buhro, "*Molecular Precursors for Electronic Materials*"
11:25 - 11:50	Talk B-1:	E. Fujita, "*Photoreduction of CO_2 using Metal Complexes*"
11:50 - 12:15 p.m.	Talk B-2:	M. Tomkiewicz, "*Revisiting the Solar Hydrogen Alternative*"
12:30 - 1:30	Lunch (Salon E and F)	

(Workshop Schedule cont.)

Tuesday, Feb. 6, 1996

1:30 - 1:55	Talk B-3:	D. Ollis, "*Application-driven Fundamental Needs in Homogeneous and Heterogeneous Photochemistry*"
1:55 - 2:20	Talk C-1:	R. Blankenship, "*Photosynthetic Antennae and Reaction Centers: Current Understanding and Prospects for Improvement*"
2:20 - 2:45	Talk C-2:	J. Miller, "*Electrons, Photons, and Molecules: Storing Energy from Light*"
2:45 - 9:30	PANEL DISCUSSIONS	
2:45 - 5:45	Panel Discussions (3:15 - 3:30 Coffee Break)	
6:00 - 7:30	Dinner (Salon E and F)	
7:30 - 9:30	Panel Discussions and Draft Report	

Wednesday, February 7 — PANEL REPORTS AND PLENARY DISCUSSIONS
Chair, A.J. Nozik

7:30 - 8:30 a.m.	Breakfast (Salon E and F)
8:30 - 10:00	6 Panel Reports by Panel Chairs (15 min. each)
10:00 - 10:30	Coffee Break
10:30 - 12:00 p.m.	Open Plenary Discussions on Panel Reports/Topics
12:00 - 1:30 p.m.	Lunch (Salon E and F)
1:30 - 3:00	Panels Meet to Discuss Feedback from all Attendees
3:00 - 3:30	Coffee Break
3:30 - 5:30	Final Summary of Panel Reports by Chairs and Final Plenary Discussion
6:00 - 7:30	Dinner (Salon E and F)
7:30 - 9:30	Panels Draft Written Report

Thursday, February 8

7:30 - 8:30 a.m.	Breakfast (Salon E and F)
8:30 - 11:30	Panels Meet to Complete Written Report

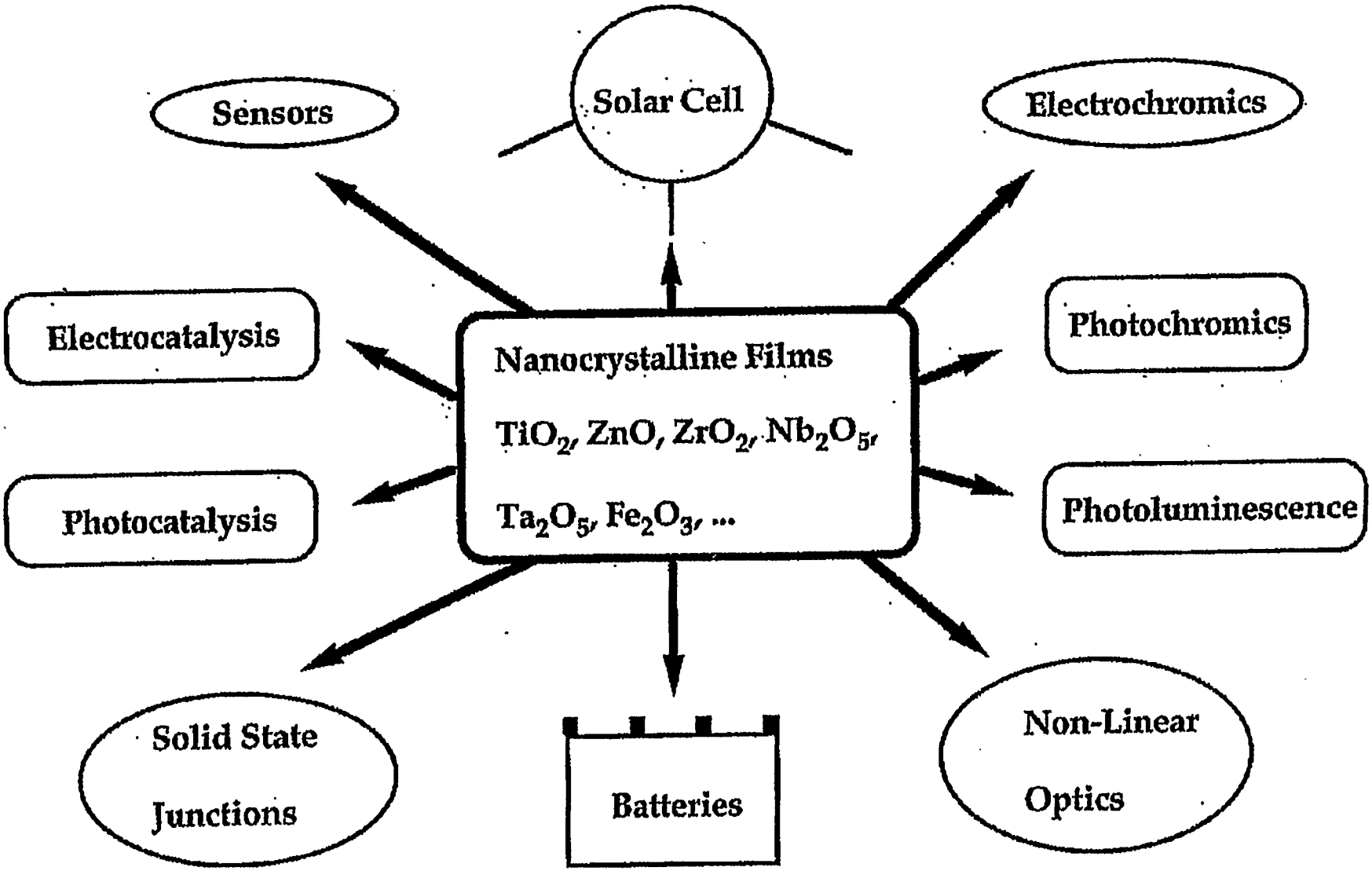


Figure 1. A summary of various applications for the new nanocrystalline electronic junctions.

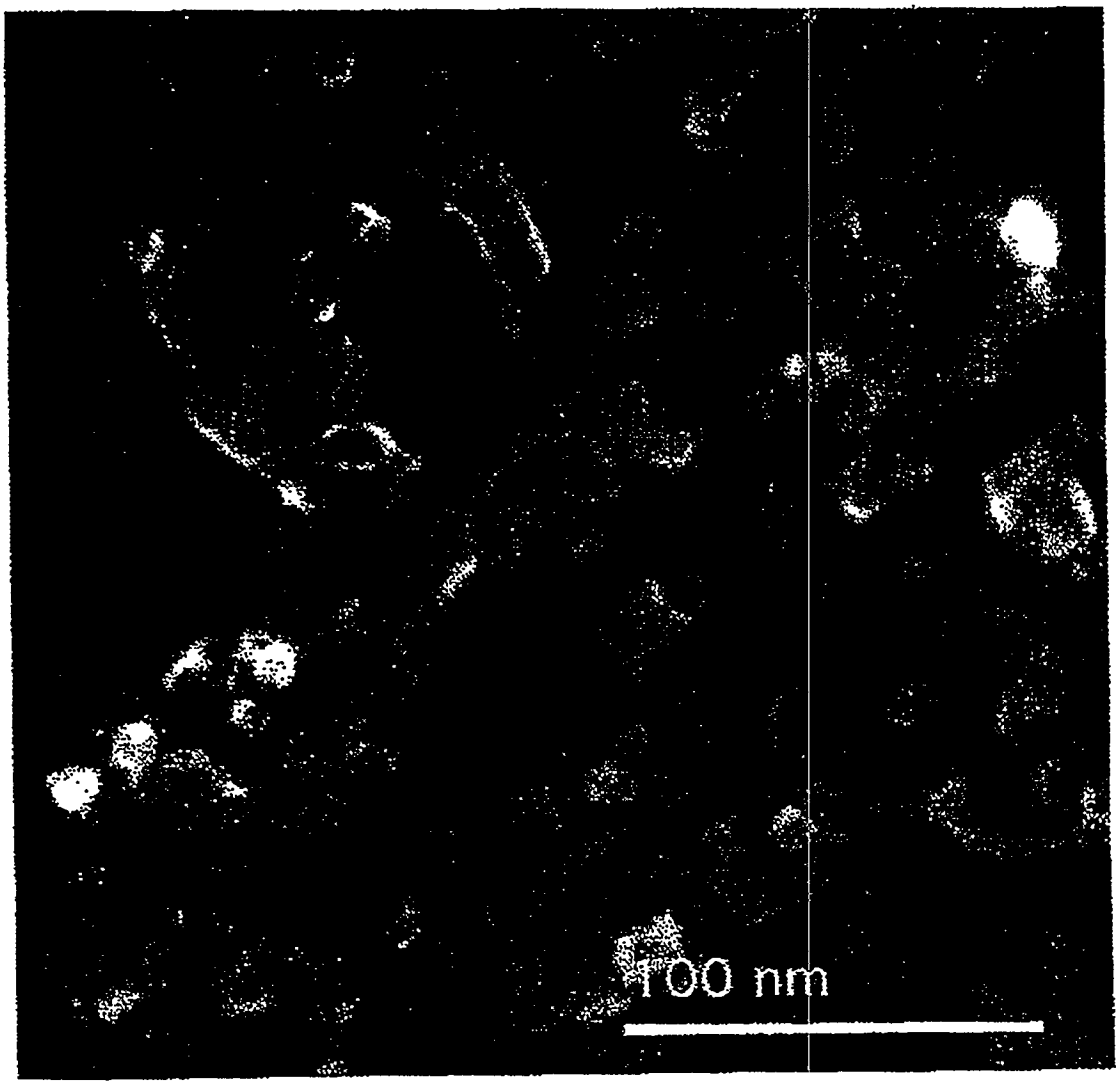


Figure 2. Scanning electron micrograph of a mesoscopic TiO_2 film.

membrane, say five micrometer thick, is only about 2 microseconds. During migration the electrons maintain their high electrochemical potential which is equal to the Fermi level of the semiconductor. Thus, the principal function of the TiO_2, apart for supporting the sensitizer, is that of charge collection and conduction. The advantage of using a semiconductor membrane rather than a biological one as employed by natural photosynthesis, is that such an inorganic membrane or film is more stable and allows extremely fast trans-membrane electron movement. The charge transfer across the photosynthetic membrane is less rapid since it takes about 100 μs to displace the electron across the 50 Å thick thylakoid layer. Moreover, nature has to sacrifice about half of the absorbed photon energy to drive the transmembrane redox process at such a rate. In the case of the semiconductor membrane, the price to pay for the rapid vectorial charge displacement is small. It corresponds to about 0.2 -0.3 V of voltage drop required to establish the electrical field in the space charge layer at the semiconductor/electrolyte junction.

The Principle of Operation of the Nanocrystalline Photovoltaic Device

The fundamental processes involved in any photovoltaic conversion process are:

- the absorption of sunlight
- the generation of electric charges by light, and
- the collection of charge carriers to produce electricity

The incident monochromatic photon to current conversion efficiency or "external quantum yield" of such a device is then given by the equation:

$$\eta_i(\lambda) = LHE(\lambda) \times \phi_{inj} \times \eta_e \qquad (1)$$

where η_i (l) expresses the ratio of the measured electric current to the incident photon flux for a given wavelength, LHE is the light harvesting efficiency, ϕ_{inj} is the quantum yield for charge injection into the oxide and η_e is the charge collection efficiency. Conventional solar cells convert light into electricity by exploiting the photovoltaic effect that exists at semiconductor junctions. They are thus closely related to transistors and integrated circuits. The semiconductor performs two processes simultaneously: absorption of light, and the separation of the electric charges (electrons and "holes") which are formed as a consequence of that absorption. However, to avoid the premature recombination of electrons and holes, the semiconductors employed must be highly pure and defect-free. The fabrication of this type of cell presents numerous difficulties, preventing the use of such devices for electricity production on a large industrial scale.

In contrast, the solar cell developed in our group at the Swiss Federal Institute of Technology operates on a different principle, whereby the processes of light absorption and charge separation are differentiated, Figure 3. Light absorption is performed by a monolayer of dye (S) adsorbed

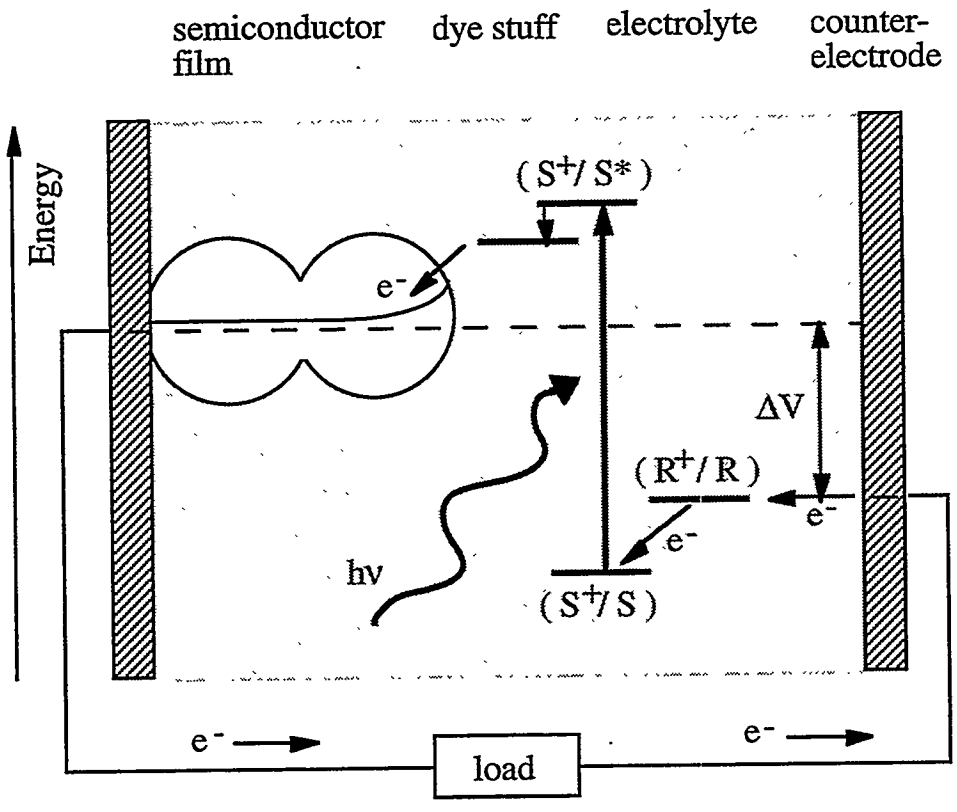


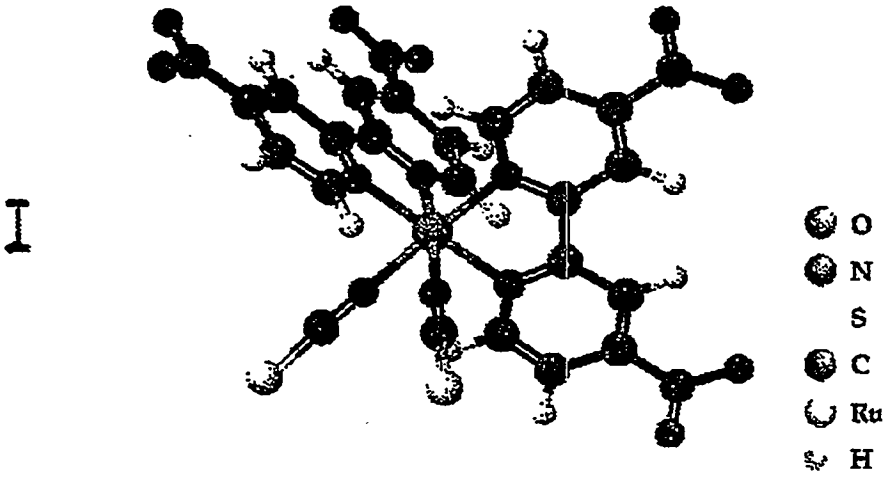
Figure 3. Schematic representation of the principle of the new photovoltaic cell to indicate the electron energy level in the different phases. The cell voltage observed under illumination corresponds to the difference in the quasi-Fermi level of the TiO_2 under illumination and the electrochemical potential of the electrolyte. The latter is equal to the Nernst potential of the redox couple (R/R^-) used to mediate charge transfer between the electrodes.

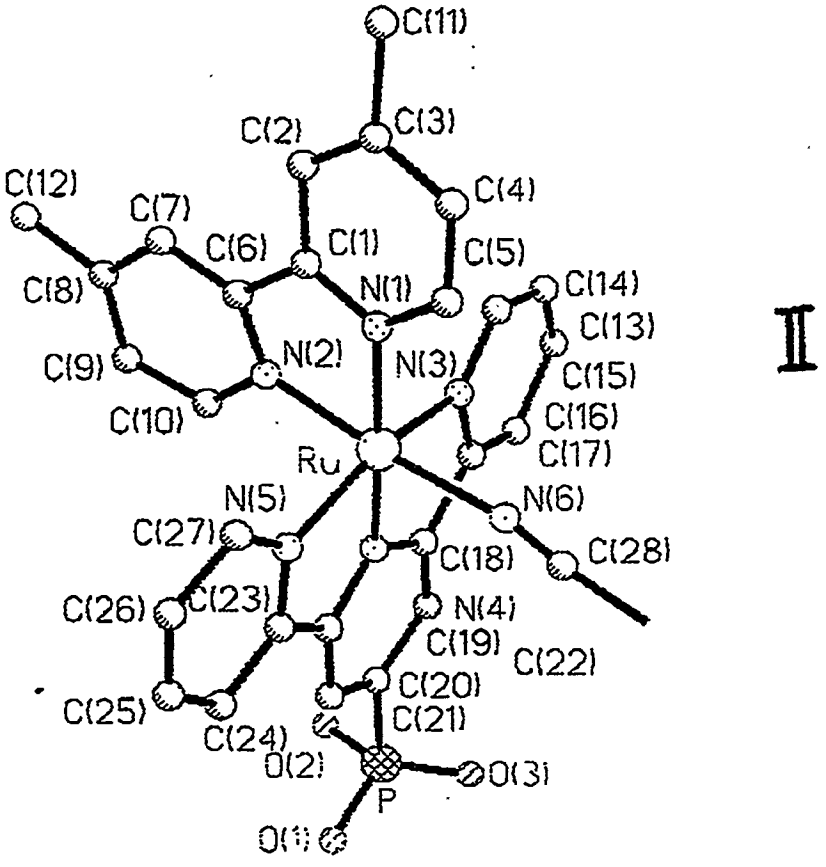
chemically at the semiconductor surface. After having been excited (S*) by a photon of light, the dye—usually a transition metal complex whose molecular properties are specifically engineered for the task—is able to inject an electron into the conduction band of the oxide semiconductor. The back reaction is intercepted by transferring the positive charge from the dye (S^+) to a redox mediator R/R^+ present in the electrolyte with which the cell is filled, and thence to the counter electrode. Via this last electron transfer, in which the mediator is returned to its reduced state, the circuit is closed. The system operates as a regenerative electrochemical cell that converts light into electricity without inducing any permanent chemical transformation. The maximum voltage DV that such a device could deliver corresponds to the difference between the redox potential of the mediator and the Fermi level of the semiconductor. The electrolyte containing the mediator could be replaced by a large band gap p-type semiconductor, e.g., cuprous thiocyanate, CuSCN [3] or cuprous iodide CuI [4]. Alternatively, a hole transmitting solid may be employed similar to the amorphous organic compounds used in electroluminescence devices. This is an attractive option which is presently being explored in our laboratory.

It should be emphasized that in all these different embodiments of the nanocrystalline injection cell minority carriers, i.e., holes in the case of an n-type conductor such as TiO_2, do not participate in the photoconversion process. This is a great advantage in comparison to conventional photovoltaic devices, where, without exception, the generation and transport of minority carriers is required. The performance characteristics of the conventional device are strongly influenced by the minority carrier diffusion length, which is very sensitive to the presence of imperfections and impurities in the semiconductor lattice. Our cell operates entirely on majority carriers whose transport is not subjected to these limitations and hence will be much less sensitive to lattice defects.

As indicated above, the absorption of light by a monolayer of dye is weak due to the fact that the area occupied by one molecule is at much larger than its optical cross section for light capture. A respectable photovoltaic efficiency cannot therefore be obtained by the use of a flat semiconductor surface but rather by use of a porous, nanostructured film of very high surface roughness. When light penetrates the photosensitized, semiconductor "sponge", it crosses hundreds of adsorbed dye monolayers. The mesoporous structure thus fulfills a function similar to the thylakoid vesicles in green leaves which are stacked in order to enhance light harvesting.

In contrast to chlorophyll, which is continuously being synthesized in the leaf, the sensitizer in the nanocrystalline cell must be selected to satisfy the high stability requirements encountered in practical applications. A photovoltaic device must remain serviceable for 20 years without significant loss of performance corresponding to a number of 50-100 million turnovers for the dye. Our work has focused on the molecular engineering of suitable ruthenium compounds which are known for their excellent stability. *Cis*-di(thiocyanato)bis(2,2'-bipyridyl)-4,4'-dicarboxylate)-ruthenium(II), **I**, was found to perform as an outstanding solar light absorber and charge-transfer sensitizer [2], which for the last five years was unmatched by any other dyestuff. Only the recently discovered Ru(II) complexes of phosphonated terpyridyl have been able to reach or even surpass the performance of **I** [5]. A structural representation of these two types of charge transfer sensitizers is shown in Figure 4.





II

Figure 4. Structural representation of two ruthenium complexes used as charge transfer sensitizers, for complex II, the crystal structure has been obtained by X-ray diffraction.

Conversion Efficiencies

The use of mesoporous oxide films to support the sensitizer allows sun light to be harvested over a broad spectral range in the visible fulfilling the first requirement for efficient light energy conversion. In order for the device to deliver a photocurrent that matches the performance of conventional cells, both the electron injection and charge carrier collection must in addition occur with an efficiency close to unity. The quantum yield of charge injection (ϕ_{inj}) is the fraction of the absorbed photons which are converted into electrons injected in the conduction band. Charge injection from electronically excited sensitizer into the conduction band of the semiconductor is in competition with other radiative or radiationless deactivation channels. Taking the sum of the rate constants of these nonproductive channels together as k_{eff} results in:

$$(\phi_{inj}) = k_{inj}/(k_{eff} + k_{inj}) \qquad (2)$$

One should remain aware that the deactivation of the electronically excited state of the sensitizer is generally very rapid. Typical k_{eff} values lie in the range from 10^3 to 10^{10} sec^{-1}. To achieve a good quantum yield, the rate constant for charge injection should be at least 100 times higher than k_{eff}. That means that injection rates in the picosecond range have to be attained. In fact, in recent years sensitizers have been developed that satisfy these requirements. These dyes should incorporate functional groups ("interlocking groups") as for example carboxylate or phosphonate groups attached to the pyridyl ligands in figure 4 which besides bonding to the titanium dioxide surface, also effect an enhanced electronic coupling of the sensitizer with the conduction band of the semiconductor. The electronic transition is of MLCT (metal to ligand charge transfer) character, figure 5, which serves to channel the excitation energy into the right ligand, that is the one from which electron injection into the semiconductor takes place. With molecules like these the injection times are in the pico- or subpicosecond range [6,7] and the quantum yield of charge injection generally exceeds 90%.

As the last step of the conversion of light into electrical current, a complete charge separation must be achieved. On thermodynamic grounds, the preferred process for the electron injected into the conduction band of the titanium dioxide membrane is the back reaction with the sensitizer cation, Fig. (5). Naturally, this reaction is undesirable, since instead of electrical current it merely generates heat.

For the characterization of the recombination rate an important kinetic parameter is the rate constant k_b. It is of great interest to develop sensitizer systems for which the value of k_{inj} is high and that of k_b low. Fortunately, for the transition metal complexes we use, the ratio k_{inj}/k_b is often greater than 10^6, which significantly facilitates the charge separation. The reason for this behavior is that the molecular orbitals involved in the back reaction overlap less favorably with the wavefunction of the conduction band electron than those involved in the forward process. For example for our Ru-complexes bound to the titanium dioxide membrane, the injecting orbital is the π^* wavefunction of the carboxylated bipyridyl ligand since the excited state of this sensitizer has a metal to ligand charge transfer character. The carboxylate groups interact directly with the surface Ti(IV) ions resulting in

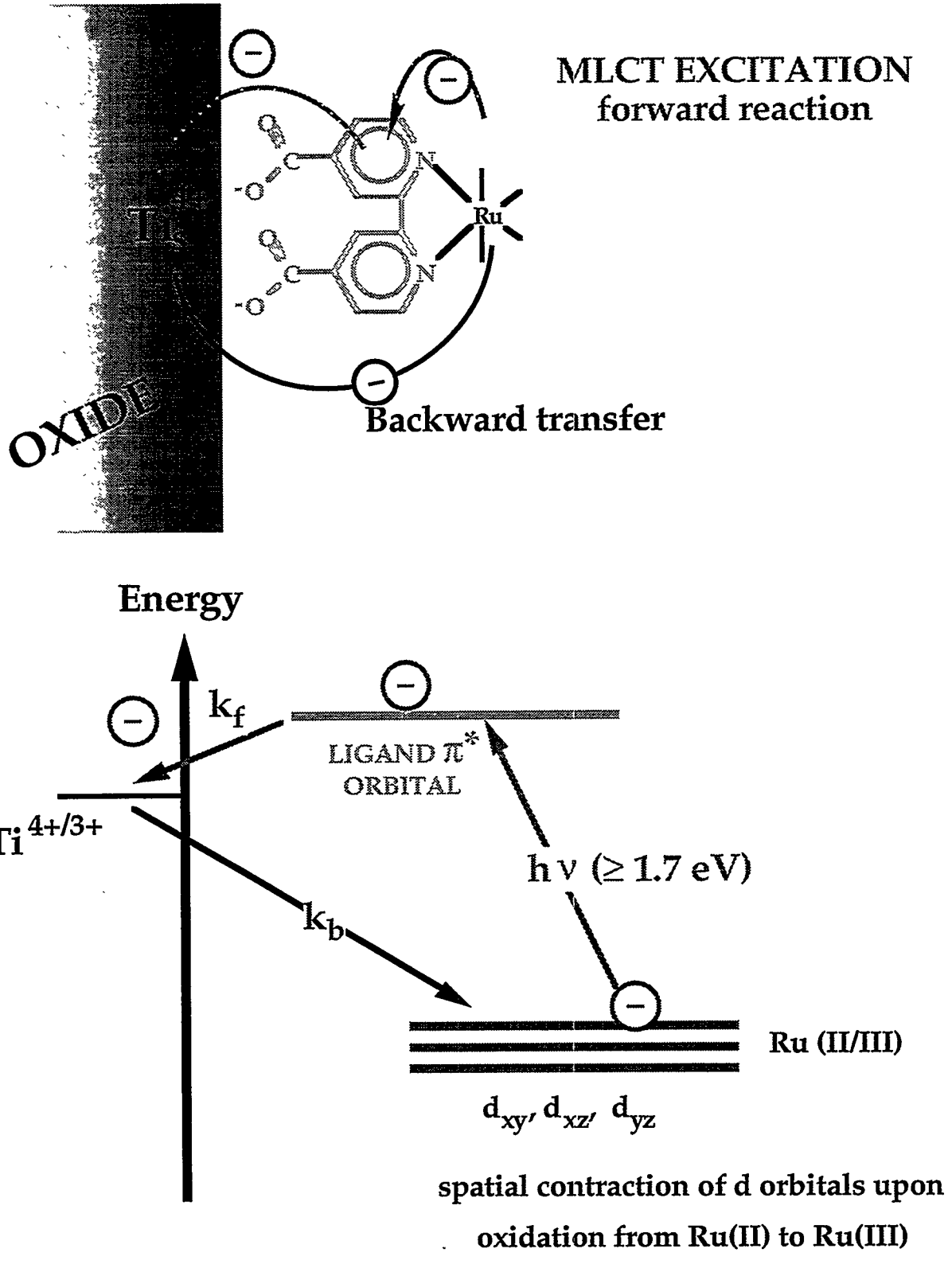


Figure 5. Energy diagram showing the electronic orbitals involved int he MLCT excitation of the Ru(II) complex attached to the surface of the semiconducting oxide via carboxylated bipyridyl groups.

good electronic coupling of the π^* wavefunction with the 3d orbital manifold of the conduction band of the TiO_2. As a result, the electron injection from the excited sensitizer into the semiconductor membrane is an extremely rapid process for which the rate constant is at least 10^{12} s^{-1}. By contrast, the back reaction of the electrons with the oxidized ruthenium complex involves a d-orbital localized on the ruthenium metal whose electronic overlap with the TiO_2 conduction band is small and is further reduced by the spatial contraction of the wavefunction upon oxidation of the Ru(II) to the Ru(III). In addition, electron recapture by the oxidized sensitizer due to the large driving force is in often in the inverted Marcus region providing another explanation for the large difference between the forward and backward electron transfer rates.

Of great significance for the inhibition of charge recombination is the existence of an electric field at the surface of the titanium dioxide film. While there is practically no depletion layer within the oxide due to the small size of the particles and their low doping level [9] a surface field is established spontaneously by proton transfer from the protonated carboxylate or phosphonate groups of the ruthenium complex to the oxide surface producing a charged double layer. If the film is placed in contact with a protic solvent the latter can also act as proton donor. In aprotic media, Li^+ or Mg^{2+} which are potential determining ions for TiO_2 [10] may be used to impose the desired positive surface charge. This local potential gradient drives the injection in the desired direction, i.e., from the negatively charged sensitizer into the positively charged oxide. The same field inhibits also the electrons from exiting the solid after injection has taken place.

The subsequent migration of electrons within the TiO_2 conduction band to the current collector involves charge carrier percolation over the mesoscopic particle network. This important process which leads to nearly quantitative collection of injected electrons is presently attracting a great deal of attention [10-12]. For example, the elegant experiments conceived by Hagfeldt and Lindquist [10] have given useful keys to the rationalize the intriguing findings made with these films under band gap illumination. The work of Hodes and Peter on nanocrystalline II-VI semiconductor films should also be mentioned here [13].

It should be noted that for the nanocrystalline injection cell there two electron loss channels one involving recombination with the sensitizer and the other reduction of triiodide ions in the electrolyte or the hole carrier present within the mesoporous network. This is summarized in the electron flux diagram in figure 6. The efficient interception of the recombination by the electron donor i.e. iodide:

$$2S^+ + 3\,I^- \longrightarrow 2S + I_3^- \qquad (3)$$

is crucial for obtaining good collection yields and high cycle life of the sensitizer. In the case of sensitizer **I**, our own time resolved laser experiments have shown the interception to take place with a rate constant of about 10^8 s^{-1} under the conditions applied in the solar cell. This is about one hundred times faster than the recombination rate and 10^8 times faster than the intrinsic lifetime of the oxidized sensitizer in the electrolyte in absence of iodide which. Cyclic voltammetry experiments carried out with solutions of **I** have shown its intrinsic lifetime in the oxidized state

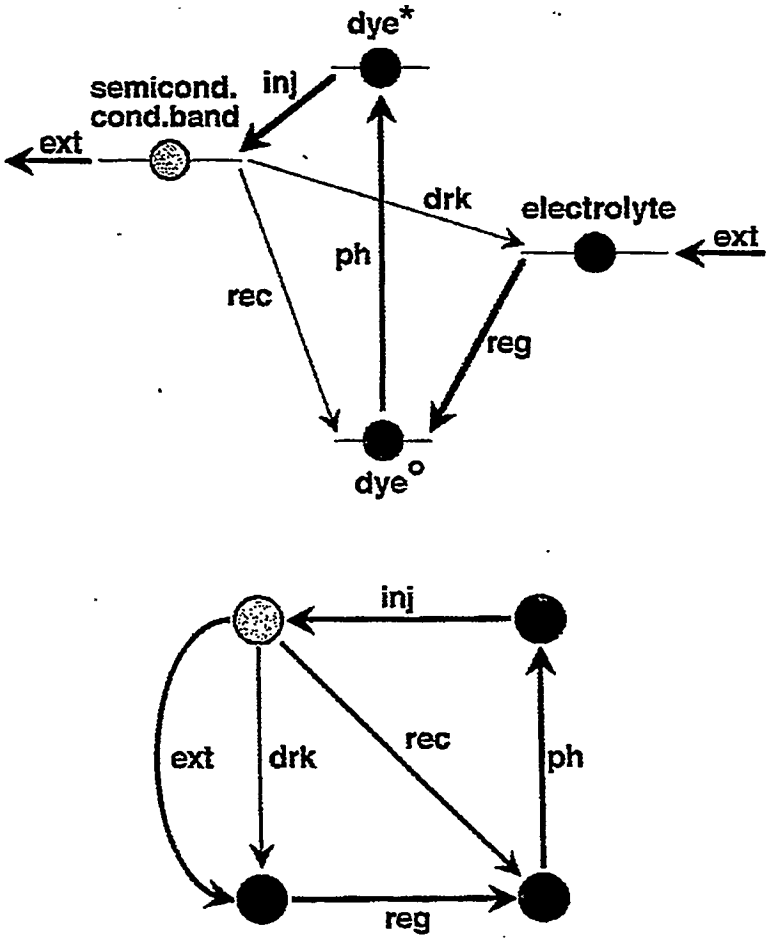


Figure 6. Diagram for the principal channels of electron flow in the injection solar cell.

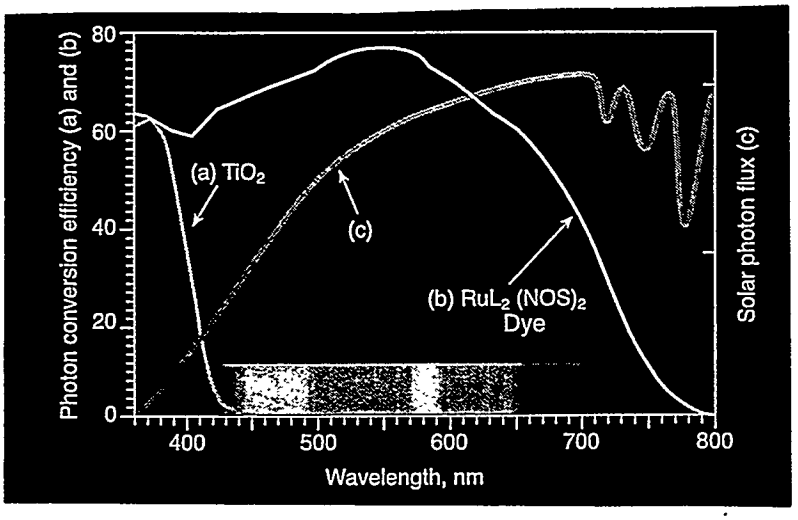


Figure 7. Photocurrent action spectrum for ruthenium based sensitizer attached to the nanocrystalline TiO_2 film. (a) The blank spectrum obtained with the bare TiO_2 surface is shown for comparison. (b) The incident photon to current conversion efficiency is plotted as a function of the wavelength of the exciting light. Curve (c) is the solar photon flux.

to be limited to about one second by intramolecular charge transfer from Ru(III) to the SCN^- group followed by irreversible oxidation of the latter ligand. The factor of 10^8 explains the fact that this sensitizer can sustain 100 million turnovers in continuous solar cell operation without loss of performance.

A graph which presents the monochromatic current output as a function of the wavelength of the incident light is known as a "photocurrent action spectrum". Figure 7 shows such spectra for three ruthenium complexes, illustrating the very high efficiency of current generation, exceeding 75% obtained with these complexes. When corrected for the inevitable reflection and absorption losses in the conducting glass serving to support the nanocrystalline film, yields of practically 100 percent are obtained. Historically, RuL_3 (L = 2,2'-bipyridyl-4,4'-dicarboxylate) was the first efficient and stable charge transfer sensitizer to be used in conjunction with high surface area TiO_2 films. In a long term experiment carried out during 1988 it sustained 9 months of intense illumination without loss of performance. However, the visible light absorption of this sensitizer is insufficient for solar light conversion. A significant improvement of the light harvesting was achieved with the trimeric complex of ruthenium whose two peripheral ruthenium moieties were designed to serve as antennas (14). An even more successful charge transfer sensitizer is *cis*-dithiocyanatobis(2,2'-bipyridyl-4,4'-dicarboxylate)-ruthenium(II). This achieves close to quantitative photon to electron conversion over the whole visible range (2). Even at 700 nm current generation is still 40-60 percent efficient depending on the thickness of the film.

The overall efficiency (η_{global}) of the photovoltaic cell can easily be calculated from the integral photocurrent density (i_{ph}), the open-circuit photovoltage (V_{oc}), the fill factor of the cell (ff) and the intensity of the incident light (I_s).

$$\eta_{global} = i_{ph} \times V_{oc} \times ff/I_s \qquad (4)$$

Figures 8 and b give examples for the current-voltage characteristics nanocrystalline injection cells based on sensitizer **I**, as measured in the photovoltaic test laboratory at the National Renewable Energy Laboratory (NREL) in Colorado USA. The photocurrent obtained at 1000 mW/cm^2 of simulated AM 1.5 global solar intensity was 18.37 mA/cm^2 the open circuit voltage was 0.762 V, and the fill factor was 0.60 yielding for the conversion efficiency of the cell a value of 8.51%. At 500 W/m^2 the fill factor increased to 0.69 and the overall yield to 9.25%. Under optimal current collection geometry, minimizing ohmic losses due to the sheet resistance of the conducting glass resistance, cells with very high fill factors, i.e., ff = 0.8 have already been fabricated. Overall conversion efficiency for AM 1.5 sunlight as high as 10.7% have been obtained, albeit at reduced, i.e., 100 W/m^2 solar AM 1.5 irradiance.

This yield is still significantly below the value of 33 percent corresponding to the upper limit for conversion of standard AM 1.5 solar radiation to electricity by a single junction cell. The main reason for the difference is the mismatch in the redox level of the dye and that of the iodide/triiodide redox system used as electrolyte, leading to a voltage loss of 0.7 V. Adjusting the redox levels to reduce this loss to a more reasonable figure of 0.3 V would allow to double the overall conversion

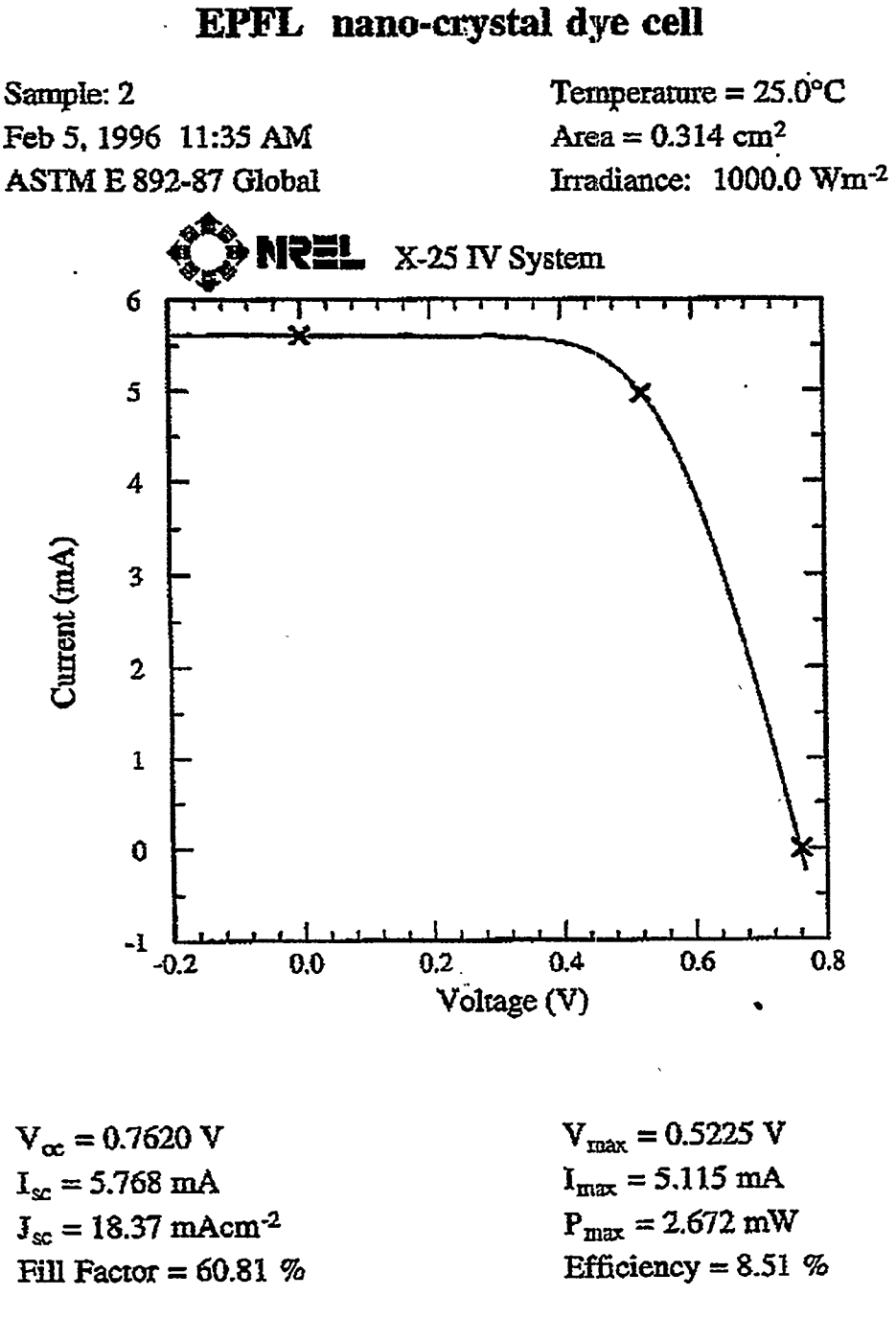


Figure 8. a) photocurrent voltage curve for a sealed nanocrystalline injection cell based on *cis*-Ru(2,2,-bipy-4,4'-dicarboxylate)$(SCN)_2$ as a sensitizer, measured and certified by the National Renewable Energy Laboratory (NREL), Golden, Colorado (USA). Simulated AM 1.5 global solar light 1000 W/m^2. b) conditions as in (a) except that the light intensity was 500 W/m^2.

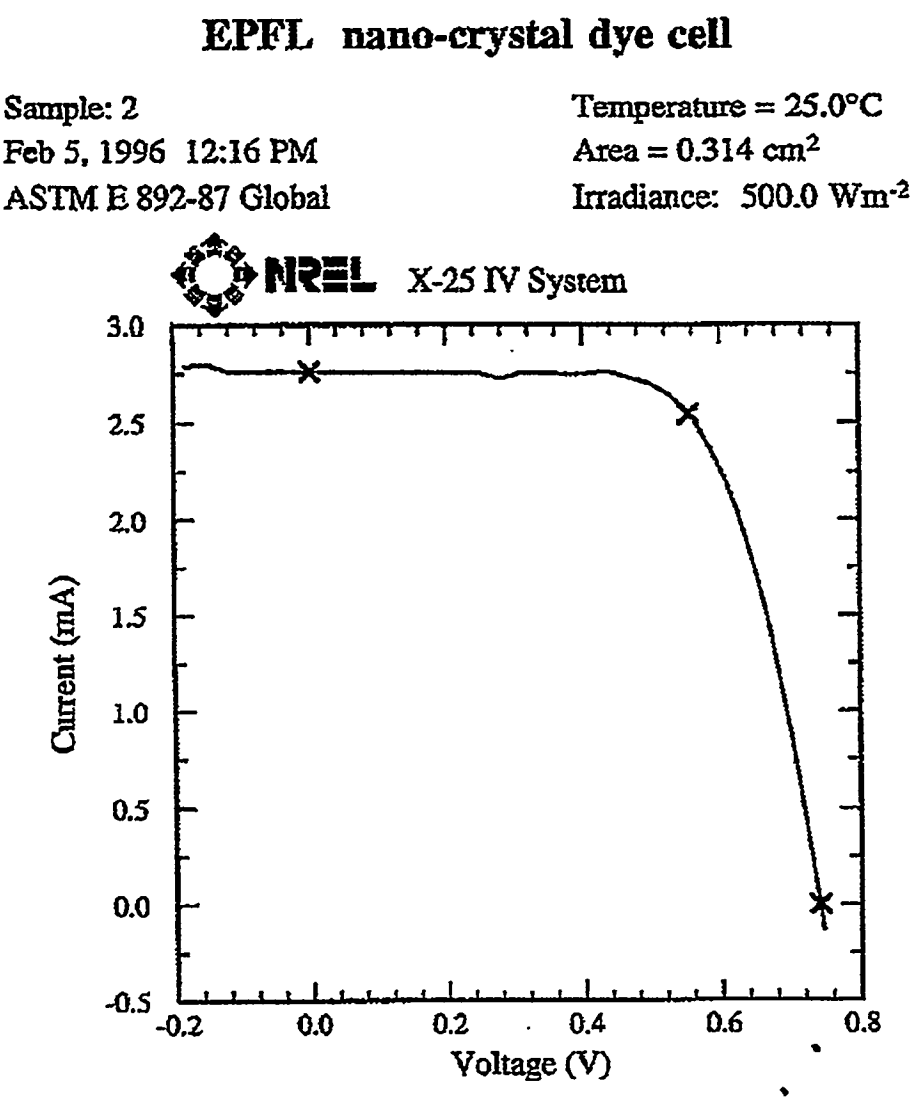


Figure 8. a) photocurrent voltage curve for a sealed nanocrystalline injection cell based on *cis*-Ru(2,2,-bipy-4,4'-dicarboxylate)$(SCN)_2$ as a sensitizer, measured and certified by the National Renewable Energy Laboratory (NREL), Golden, Colorado (USA). Simulated AM 1.5 global solar light 1000 W/m^2. b) conditions as in (a) except that the light intensity was 500 W/m^2.

efficiency from 10 to 20 percent. An improvement of the cell current by ca 30% should be possible through better light harvesting in the 700 to 800 nm range where the absorption of **I** is relatively weak. Applying a dye cocktail which is complementary in spectral response offers a straightforward way to achieve this goal. Thus it is feasible to reach with nanocrystalline materials efficiencies around 25%, which falls in the same range as that observed with top quality, single crystal GaAs solar cells.

An advantage of the nanocrystalline solar cell with respect to solid state devices is that its performance is remarkably insensitive to temperature change. Thus raising the temperature from 20 to 60 °C has practically no effect on the power conversion efficiency. In contrast conventional silicon cells exhibit a significant decline over the same temperature range amounting to ca 20 percent. Since the temperature of a solar cell will reach readily 60 °C under full sunlight, this feature of the injection cell is particularly attractive for power generation under natural conditions.

Development of in Series Connected Modules and Stability Tests

Meanwhile, the development and testing of the first cell module for practical applications has begun. The layout of the module is presented in Fig. 9. The cell consists of two glass plates, which are coated with a transparent conducting oxide (TCO) layer. The nanocrystalline titanium dioxide film deposited on one plate functions as a support for the ruthenium complex acting as charge transfer sensitizer. On illumination, this injects an electron into the titanium dioxide conduction band. The electrons pass over the collector electrode into the external current where they perform work. They are then returned to the cell via the counter electrode. The sensitizer film is separated from the counter electrode by the electrolyte containing the redox couple, for example triiodide/iodide, whose role is to transport electrons from the counter electrode to the sensitizer layer. A small amount of platinum (5-10 $\mu g/cm^2$) is deposited onto the counterelectrode to catalyze the cathodic reduction of triiodide to iodide.

A alternative approach developed by Dr. A Kay in our laboratory uses a monolithic triple layer structure Figure 10 where the nanocrystalline anatase film, a porpous spacer and the carbon counterelectrode are directly deposited on top of each other. A 21 cm^2 sized working interconnected module consisting of 6 Z-type interconnected cells was demonstrated during the lecture. Accelerated stability tests performed with this type of cell are shown in Figure 11. Continuous exposure to full sunlight for 100 days did not result in any significant deterioration of performance.

Meanwhile, the stability of all the constituents of the nanocrystalline injection solar cells, that is, the conducting glass the TiO_2 film, the sensitizer, the electrolyte, the counterelectrode and the sealant has been subjected to close scrutiny. The TCO glass and TiO_2 being unquestionable investigations have focused on the four other components. Upon long time illumination, complex **I** sustained 10^8 redox cycles without noticeable loss of performance corresponding to ca. 20 years of continuous operation in natural sunlight. By contrast, practically all organic dyes tested so far underwent photo-bleaching after less than 10^6 redox cycles. This clearly outlines the exceptionally stable operation of the newly developed transition metal charge transfer sensitizers which is of great advantage for

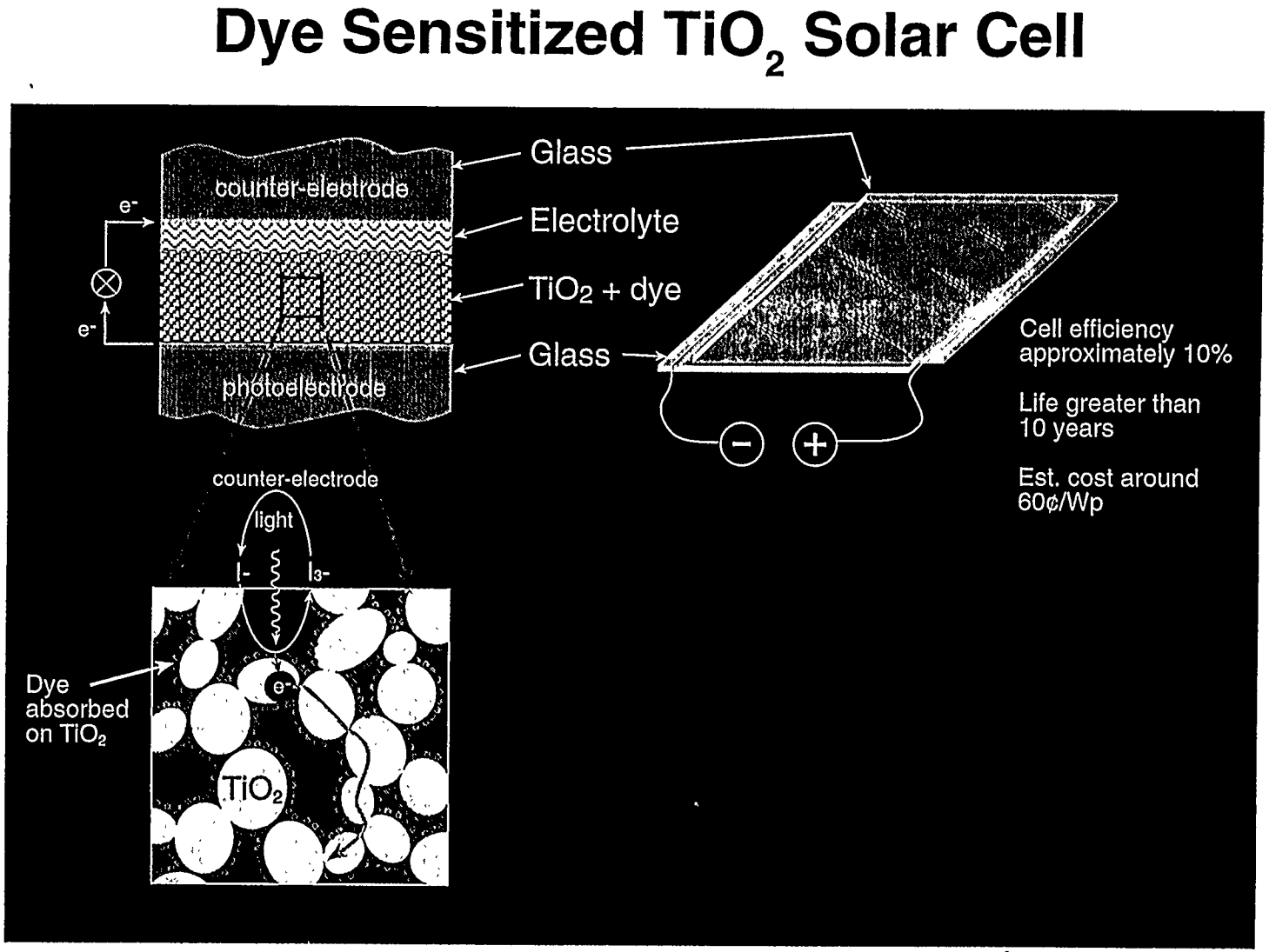
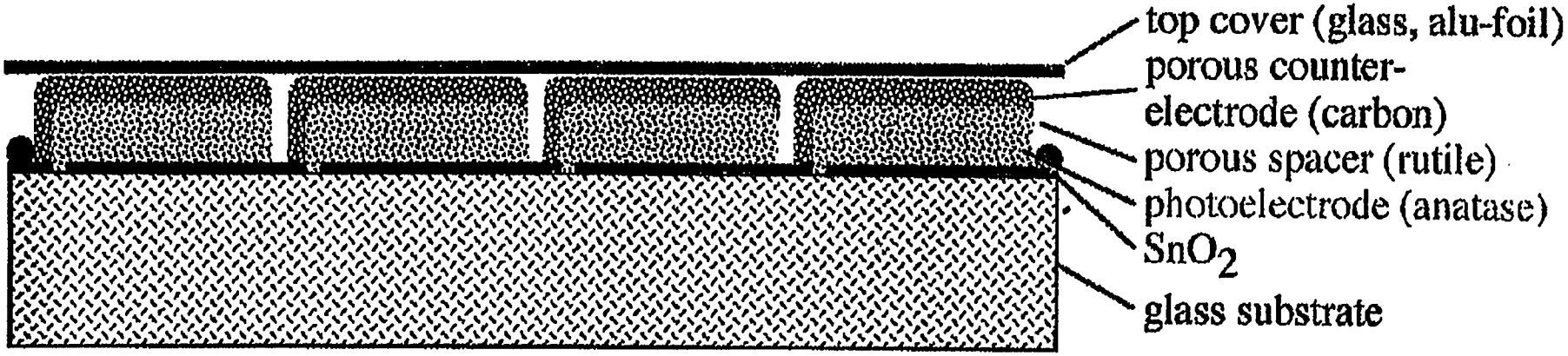


Figure 9. Lay out of a nanocrystalline solar cell. The photoactive film is sandwiched between two conducting glass sheets.

Monolithic, series-connected, dye-sensitized photovoltaic module



Advantages:

1. Only one expensive SnO_2 coated glass substrate needed
2. Minimal electrode separation independent of substrate flatness
3. Insulating spacer acts at the same time as diffuse reflector
4. Electrolyte fixed by capillary forces in the porous coatings
4. High catalytic activity of counter electrode due to high surface area
5. Series connection of many cells in Z-configuration by simple overlap of electrodes
6. Porous counter electrodes allow application of heat and humidity sensitive dye and electrolyte after fabrication of electrodes and interconnections
7. Top cover only serves to seal cell but has no electrical function

Figure 10. Structure of the first monolithic Z-type in series connected PV module made from injection cells using a three layer structure consistency of a nanocrystalline anatase film, a porous spacer, and a carbon counter electrode.

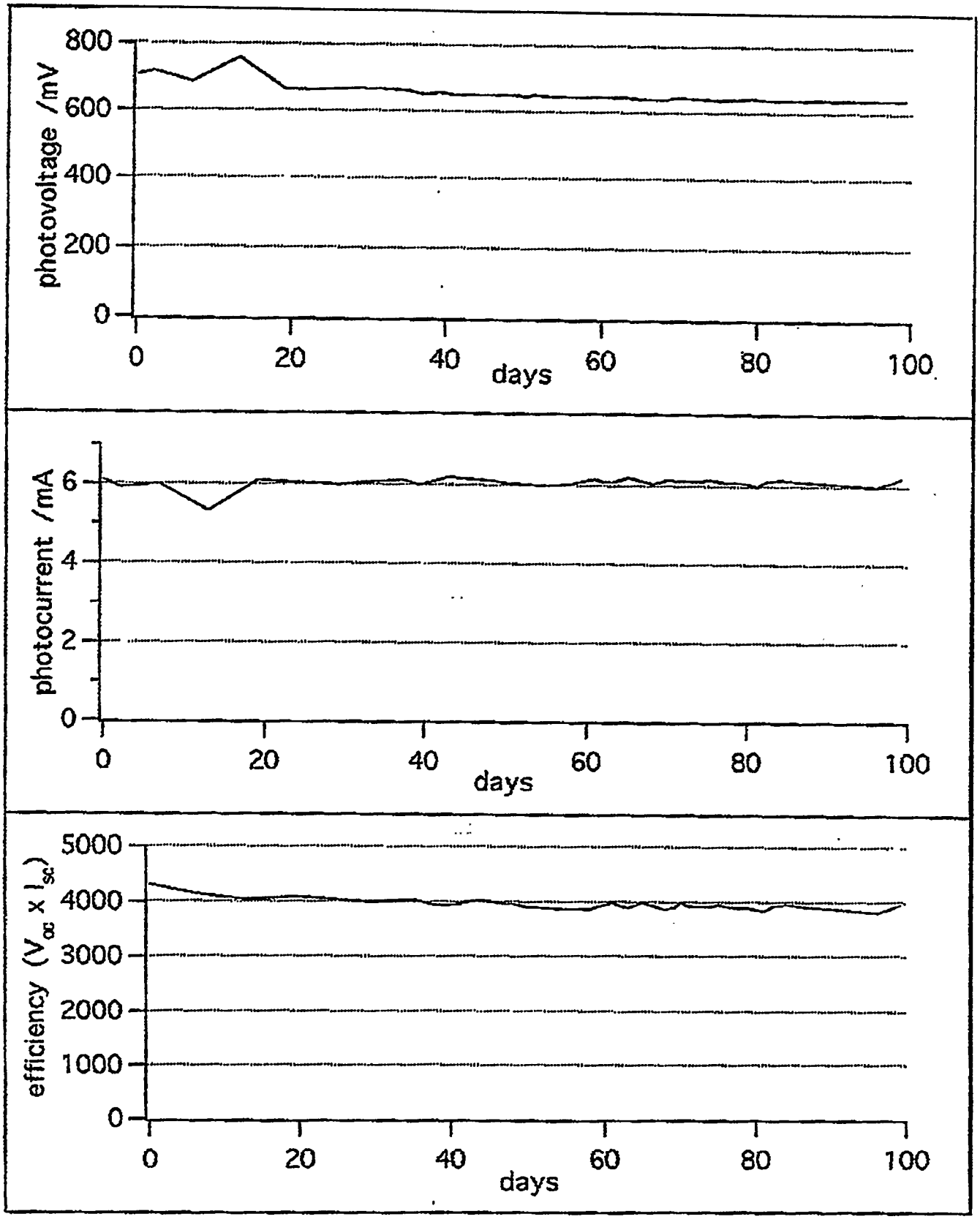


Figure 11. Accelerate aging test of a sealed nanocrystalline injection solar cell (area 0.44 cm^2). The cell was continuously exposed to simulated AM 1.5 sunlight during 100 days. Cell temperature was about 60°C. UV light was filtered.

the practical application of these devices. The reason for this amazing stability is the very rapid deactivation of the excited triplet state via charge injection into the TiO_2 which occurs in the femtosecond time domain. This is at least 8 orders of magnitude faster than any other competing channel of excited state deactivation including those leading to chemical transformation of the dye.

Stability tests on sealed cells have progressed significantly over the last few years. These tests are very important, since—apart from the sensitizer—other components of the device, such as the redox electrolyte or the sealing, may fail under long term illumination. Indeed, a problem emerged with electrolytes based on cyclic carbonates, such as propylene- or ethylene carbonate, which were found to undergo thermally activated decarboxylation in the presence of TiO_2 rendering these solvents unsuitable for practical usage. They were therefore replaced by a highly polar and nonvolatile liquid which does not exhibit this undesirable property. More recently, room temperature molten salts based on imidazolium iodides and triflates have revealed very attractive stability features. Thus, fully assembled cells showed no decline in photovoltaic performance, i.e., photocurrent, photovoltage and fill factor, when submitted to accelerated aging performed in a sun test (AM 1) chamber at 44 °C and 85 °C for at least 2300 hours and 1000 hours, respectively. Direct excitation of electron hole pairs in the anatase by $\lambda > 380$ nm light was avoided in these experiments by using a polycarbonate protective film.

Cost and Environmental Compatibility of the New Injection Solar Cell

Several industrial sources, including Asea Brown Boveri, Strategies Unlimited and Research Triangle Institute, have performed a cost analysis which yields 0.6 US$/pW and 2000 US$/kWp for module and total systems cost, respectively. Similar values were reported by Smestad (15).

It may be argued that the presence of ruthenium renders the price of the sensitizer too high for commercial exploitation or that there is insufficient supply of it. However, the required amount of ruthenium is only 10^{-3} moles/m^2 of ruthenium complex corresponding to the small investment of ca. US $ 0.05/m^2 for the noble metal. The world trade in ruthenium reached 10 tons in 1994 mainly due to its use as dimensionally stable anode in electrochemical chlorine production. One ton of ruthenium alone incorporated in the charge transfer sensitizer **I** could provide one gigawatt of electric power under full sunlight. This is more than twice the total photovoltaic capacity presently installed worldwide. Thus the cost and supply of ruthenium based sensitizers is of no real concern here. The price determining factor for this photovoltaic technology is undoubtedly the conducting glass.

Apart from efficiency and stability, any future photovoltaic technology will be valued according to its environmental and human compatibility. There is great concern about the adverse environmental effects and acute toxicity of CdTe or $CuInSe_2$ which are being considered for practical development as thin solar cells. Such concerns are unjustified for our nanocrystalline device. Titanium dioxide is a harmless environmentally friendly material, remarkable for its very high stability. It occurs in nature as ilmenite, and is used in quantity as a white pigment and as an additive in toothpaste. Worldwide annual production is in excess of 1 million tons. Similarly, ruthenium has been used

without adverse health effects as an additive for bone implants. Quite aside from its intrinsic merits as a photovoltaic device, the sensitized nanocrystalline photovoltaic device will undoubtedly promote the acceptance of alternative energy technologies, not least by setting new standards of convenience and economy for the photovoltaic industry as a whole.

Nanocrystalline Intercalation Batteries

The diffuse and intermittent nature of sunlight renders necessary the storage of solar energy in electrical or chemical form. There is presently a thrive for improved batteries effecting electric energy storage. In this context the so-called "rocking chair" batteries deserve particular attention. Electric power generation is associated with the migration of lithium ions from one host , i.e. TiO_2 , constituting the anode, to another host electrode, i.e. NiO_2/CoO_2 or MnO_2, constituting the anode. The voltage delivered by the device is simply the difference of the chemical potential of lithium in the two host materials. It was discovered in our joint research with Dr. Exnar from Renata Corporation and Dr. Randin from Asulab that the intercalation of lithium is greatly facilitated if the oxides employed have a nanocrystalline morphology as compared to bulk electrodes. Thus, for TiO_2 the capacity for Li^+ uptake is increased by a factor of roughly two and the intercalation and the release of the ions is much faster than for bulk materials. The reason for this behavior is that the diffusion time for lithium ions in the host oxide is dramatically shortened by using oxide particles of mesoscopic dimensions as electrodes. A standard size R921 coin cell has been developed supplying 5 mAh corresponding to 50 mAh/g capacity which compares well with the rocking chair battery having a carbon anode. These findings provide a very promising basis for the development of a new type of rechargeable battery (16).

In conclusion, it appears that nanocrystalline electronic junctions involving transition metal oxides form not only the heart of a new photovoltaic device but offer also attractive perspectives for the storage of electrical energy that is generated by sunlight.

Acknowledgment

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A CRITICAL TEST OF ORGANIC P-N PHOTOVOLTAIC CELLS

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Abstract

We present an urgent view of the field of organic solid state photovoltaic cells. This is a proper time to select the most promising materials from the Electrophotographic Industry, materials long tried in terms of stability, high quantum yield of charge carriers, but set apart by unusually high quantum yields at low applied fields. Unfortunately, our experience has been uniformly unhappy with the state of basic knowledge covering identity, purity, and interference from polymorphs: coexisting multiple crystal forms of these otherwise-exemplary components.

Our experience with the candidate dyes has covered new tests for identifiable impurities and removal of these impurities by verifiable methods. A new method of purification, reactive train sublimation, has been developed for DMP, one of the simplest of the outstanding perylene dyes, and the method seems applicable to some of the other promising perylene derivatives. It removes the offending impurity by converting it into the desired pure product.

The role of water of hydration in the "wine cellar effect", the slowly rising performance of newly made phthalocyanine containing cells has been analyzed. Under the concept of feasibility testing before a final refinement for practicality of materials and production methods, the hydration can be controlled for high level testing. At the same time, efforts go forward to eliminate the need. At least one of the best phthalocyanine components, X-H_2Pc, does not require water for peak performance.

Finally, we have attacked BBIP (bis-benzimidazole perylene) one of the best and most enigmatic of the near infrared sensors. It has long been known and used as a mixture of synthetic isomers, and we hypothesize that either of these would be better than the uncontrolled mixture. A partial success in the form of isolating highly enriched crystals for an X-ray structure of the trans-molecule, is first presented here. A simple optical analysis method has been developed to follow enrichment procedures. For all of its difficult history, this material seems closest to a state of readiness for critical feasibility testing.

Introduction

Is it reasonable to hope that a simple and inexpensive solid state organic p-n cell may be constructed with energy efficiency adequate to justify deployment as a photovoltaic energy harvesting system? Is it possible to chart a path of sensible experiments which would lead in this direction? Such a cell might compete with amorphous silicon (1) though not directly against either single crystal silicon (2) or against future grades of polycrystalline silicon (3).

Organic p-n cells (4) might find economical use where snow avalanches or 80-100 mph sand storms may occasionally destroy quantities of cells. At this moment, the question of ultimate utility can't be answered even for the most promising pairs of organic p-n cell components, because the critical information has never been collected. Here we will consider a division of that question into a feasibility test of energy efficiency and durability and a second question of cost of production and field flexibility. The feasibility test is closer to us than the practicality question as a result of neglected materials unknowns. An attack on these will require a step upward in sophistication to make full use of present modeling and structure predictions coming out of advanced protein and DNA crystallography (5) and out of quantum mechanical calculations (6) of increasing validity.

Comparison of Solid-State OPV Cells with TiO_2/Bis-2,2'BipyridylRutheniumI-Bis-$(SCN)_2^+/H_2O$ Cells

The question posed here for the solid state organic systems has already been answered in large part for the metal-organic systems advanced by Grätzel and coworkers (7a,b,c). These systems involve bis-2,2'Bipyridyl-bis-thiocyanato complexes of Ruthenium^{++}, with the assembled complex being bonded to colloidal TiO_2 in a water host and contact. These systems have already shown parameters of charge carrier quantum yield, open circuit voltage and fill factor which make them serious contenders for practical energy harvesting applications. It isn't yet quite clear just where the advantages of this class of systems will lead, but they certainly will have applications.

Perhaps it will help a bit if we focus on the contrasts between the Rutheniumbipyridyl-based systems (RuBipy for short) and the "pure" organic solid state systems (OPV). Obviously the pure organic distinction has broken down with the use of Al, Ti, Ga, and Indium Phthalocyanines. There are still at least two distinctions here, and a third distinction created by the first two. First of all, the OPV chromophores are aimed at the strong absorber class ($\epsilon = 40{,}000$) while the RuBipy is working from an absorption band of medium intensity leading to a charge-transfer state ($\epsilon = 10{,}000$). The OPV systems have always been aimed at very thin solid state layers (*ca.* 30 nm) to minimize the usual organic problems of slow charge carrier movement and trapping. The perylene (8a) and phthalocyanine dyes are not quite in the strongest classes of dyes, but do run a close second to the cyanines (8b). The bis-bipyridyl chromophore is just too short in physical length to develop a really strong visible absorption band, but its modest peak intensity is compensated by a large band breadth. Here we must consider integrals over the absorption band systems, and the basic transition dipole integral is the best to use (9):

$$I = \int_{band} \frac{\varepsilon d\lambda}{\lambda} (\text{Moles / Liter})^{-1} \text{cm}^{-1}$$

This integral can be taken on chromophores in solution and frequently transposed directly to solid state systems, in spite of a complete reshaping of the absorption band(s) of isolated molecules, though with due allowance for orientation on a substrate surface. The direct integral is multiplied by $C = 9.185 \times 10^{-3}$ to give the quantum mechanical dipole strength in Debyes^2 or by $C = 9.185 \times 10^{-39}$ to give the dipole strength or squared transition dipole in esu^{2}cm^2. The dipole strengths for a representative bis-bipyridyl Ruthenium complex and for representative Perylene and Phthalocyanine dyes are given in Table 1.

Table 1: Dipole Strengths of Prototype Compounds

Compound	Peak λ (ϵ)	Integration	Dipole Strength
$RuL_2(NCS)_2$	528nm (14,200)	800nm-450nm	30.2 D^2
CuPc	680nm (160,000)	745nm-525nm	80.1 D^2
DXP	527nm (84,600)	560nm-400nm	66.1 D^2

Data on $RuL_2(NCS)_2$ are from ref. (7b). DXP is the 2,6-dimethylaniline adduct to perylenedianhydride. It is an efficient laser dye, described in Ref. (6)

In this context, the spike-absorption band of dissolved phthalocyanines is of no interest as a peak value - rather, the spike must be and is redisposed by accidental or theoretically directed solid state packing structures and transition dipole coupling schemes to give a solid state dye absorption band covering a designed half or more of the visible spectrum. Unless the literature has confused the point, the bis-bipyridylRutheniumdi(thiocyanato)$^{+1}$ complex is not designed for close packing on a substrate surface, and one takes the absorption more or less as it resembles the monomeric complex band in solution. If so, the more modest absorption of the bipyridylRuthenium CT band sets a requirement that the TiO_2 colloid must be of the order of 10-20 particles thick. This is acceptable provided the colloidal system is a low resistance conductor.

To draw an analogy from dye sensitized photographic systems, the RuBipy system resembles an ultrafine grained holographic film which has a huge surface-to-volume ratio and can be dye sensitized in the "monomer mode" with individual dye molecules adsorbed flat-on and interacting only weakly with each other. By contrast, the solid state OPV system resembles a coarse-grained high speed film, which has a low surface-to-volume ratio (perhaps 1% of the other) and must be sensitized with ordered dye aggregates standing on one edge on the AgBr grain and packed at the minimum 3.4 Å intermolecular distance in the "J" aggregate structures. Each system has its virtues.

We should note here an unusual hybrid system (11) in which a triple deck of three absorbing and photoactive dyes is put down together: one layer of metal-free phthalocyanine and two of the preferred perylene derivatives that we will be considering in depth, DMP and BBIP. The authors of (11) did this with some background knowledge of the energy levels, which won't be available in many other cases.

The role of the metal central atom in the various favored phthalocyanine complexes with the tetradentate (inner nitrogens) metal bonding arrangement seems not to be critical in setting the redox potentials of the complexes (10). In the case of metal-free Pc (X-phase is one of the best) the core "ion" is $2H^+$, and in the case of ClAlPc it is $ClAl^{++}$. For the titanyl complexes it is OTi^{++}, as it is for OIn^{++}. The Zn^{++} complexes have a diamagnetic core and are favored for fluorescence yield in solution and for energy-conserving performance. If the charge on the core ion and the presence, absence, or position of metal electrochemical potentials seem to have so little effect, are we currently missing a major opportunity to optimize the system?

Discussion

Water

The above discussion puts the strength of absorbers and the criticality of metal atom or OPV crystal structures along a rational line. It leaves the third variable, which to our embarrassment is water! (12.) One of the implicit goals of the OPV system is to have insensitivity to environment, and absence of "wine cellar effect". This drift of ClAlPc/Perylene systems to higher performance with time of exposure to humidity levels higher than some limit (less than 40% for ClAlPc) has been observed by several groups who made cells with AlClPc or TiOPc. Now we have the proof that the effect is the uptake of two molecules of water to make $ClAlPc{\cdot}2H_2O$ or of one molecule to make $ClAlPc{\cdot}H_2O$. One can easily imagine designing organic photovoltaic systems which exist in equilibrium with a co-packaged humidistat system. The humidistat mixture can be a superficially dry system of two related hydrate salts. However, linear control is available through the simple hydrostating mixtures of 1:1 MX salts with their own saturated solutions M^+X^-. The worry is that under desert conditions the system would pass rapidly from hot and sunlit (*ca.* 60C) to rapid radiative cooling at night (+5 to -5C) and back to sunlit and hot with a speed that might outrun the rates of change within the panel assembly. The most encouraging finding (which must be checked) is the supposition that several systems of BBIP and substituted BBIP compounds are giving high level response as potential OPV materials, presumably without benefit of "adsorbed water".

Choice of Dye Families for OPV Cells

We have reached a stage of development in which the sheer synthetic proliferation of new p- or n-dyes at the level of 200/year or even 2000/year does not seem to be a profitable mode of attack. Earlier work has largely eliminated the merocyanines and the squaric acid dyes (13a, 13b) but left the porphyrins in active candidacy (14a, 14b, 15). There is a small body of unusually stable candidate organic photovoltaic cell materials which should, if properly handled and optimized,

begin to close on the ultimate questions of practicality. These are the phthalocyanine dyes and the perylenes, representing peak stability materials. These have been extensively screened for applications as sensitizers of practical electrophotographic (EP) systems, but tested with applied electrical fields up to 1000 V/.0025 cm. This level of testing is more forgiving than any reasonable test of an organic photovoltaic (OPV) material, considering that the designed internal field is limited to about 50% of the lower band gap of a candidate p-n pair. The OPV candidate materials must give a high quantum yield of charge carriers per incident photon, and this yield must be approached at notably low fields. One can quickly generate a "short list" of OPV candidates from the notable low field photoconductors of electrophotography, as shown in Table 2. This is the easy part of the selection.

Table 2: Select Dyes from Electrophotography

PHTHALOCYANINES	PERYLENES
X-H_2Pc, X-Phase Metal-Free Phthalocyanine	DMP: DiMethylimide of PeryleneTetra CarboxylicAcid
Y-ClAlPc·2H_2O, Chloro-Aluminum Pc	DPP DiphenylImide of PeryleneTetra CarboxylicAcid
ZnPc, Zinc Pc	BBIP "BisBenzimidzole Perylene See Figure 4
MgPc, Magnesium Pc	
Y-TiOPc·H_2O Y-Phase Titanyl Pc	

Stability of Photovoltaic Materials

Stability of organic dyes is always a serious question. There is a major gain in passing from dyes in monomeric solution to "pigments", which are actually microcrystalline suspensions of dyes in some non-solvent plastic matrix or "vehicle". One thinks of thin evaporated or solvent-cast layers in this same class. Again, one looks to the perylene and phthalocyanine families and finds asphalt roofing shingles dyed blue and automobiles in the German Army lacquered dark brown with these materials. Another sign of high stability is prominence of the parent molecular mass as the most abundant + ion in mass spectrometry with energetic electron bombardment, often at 70 eV giving:

$$M_o + e^-(70\ eV) \rightarrow M_o^+ + 2e^-$$

A very strong indication of stability is shown by dyes which survive and retain crystal order for several days in air in the concentrated X-ray beam of a diffractometer. Another indication of stability is the opportunity to purify the material by Train Sublimation (entrainment of the monomeric vapor

in a hot inert flowing gas such as N_2, CO_2, or Argon). The success of train sublimation assures the subsequent fabrication of thin layers in practical p-n configuration by vacuum evaporation. The ultimate manufacture of such cells could employ the milder treatment of solvent casting, as in the manufacture of highly uniform eight or nine layer coatings for color films. Thus surviving train sublimation is supportive but not absolutely mandatory as a test for candidate OPV materials. We and others practice train sublimations (16) at 420-520C, and occasionally switch off the room lights to remind ourselves that this is "red hot organic chemistry". We'll now consider this level of stability, as it interacts with the attainable level of purity of organic dyes-as a favorable sign, along with the more formal requirements of facile photoionization, high exciton migration, and strong dye absorption. Secondary desirable features may include general low solubility, high melting point, and low reactivity with environmental pollutants O_3 and NO_2, though these pollutants are hopefully to be diminished by widespread future use of solar energy.

Stability *versus* Purity

It may almost seem that the workers in the field of OPV cells have weighed durability too heavily in selecting this generation of candidate materials. The most stable and invariant materials have been chosen, in spite of some obvious difficulties. For example, it would be helpful to be able to zone refine or at least to recrystallize some of the best OPV dyes just to make sure that impurities are not limiting the performance of the best of the trial cells. If the search for the most helpful materials has led us to two classes of dyes which don't melt and don't dissolve well even in hot solvents, then so be it! In the use of such drastic methods of purification as train sublimation, one can lose sight of the need for the sole method of purification to be highly effective. We noted early that closely similar materials might fall within a single condensation zone, since the zone of each material has a sharp high temperature edge, but tails away over distances on the order of 10 cm. Here one begins to wonder about the purity of DMP (the adduct of two moles of methylamine CH_3NH_2 with the dianhydride of perylene 3,4,9,10-tetracarboxylic acid). This final product is so insoluble that we have yet to find a reference to recrystallization of DMP. Some PV investigators have thrice train sublimed this material without commenting on the implied improvement in purification. We'll now examine the probable futility of multiple train sublimations and show how to deal with a persistent class of impurities in some or many of the perylene derivatives. Note that one of the almost unique advantages of DMP seems to be the absence of polymorphs, which are multiple distinct crystal structures, only one of which is normally thermodynamically stable. These polymorphs impact on the need for high exciton mobility by imposing phase boundaries where none are needed. We require that long-lived devices be made with the stable polymorph, however difficult it is to make directly into controlled thin coatings.

Purification of Perylenes, DMP as an Illustration

The mass spectra and the synthetic route to form DMP are shown in Figure 1. Even if the synthesis were to be done with anhydrous methylamine (readily available in cylinders), water, formed as a reaction product, is made available, and can react rapidly with anhydride functions of the major starting material. We suspected that the 3,4-monoimide-9,10-dicarboxylic acid would dehydrate

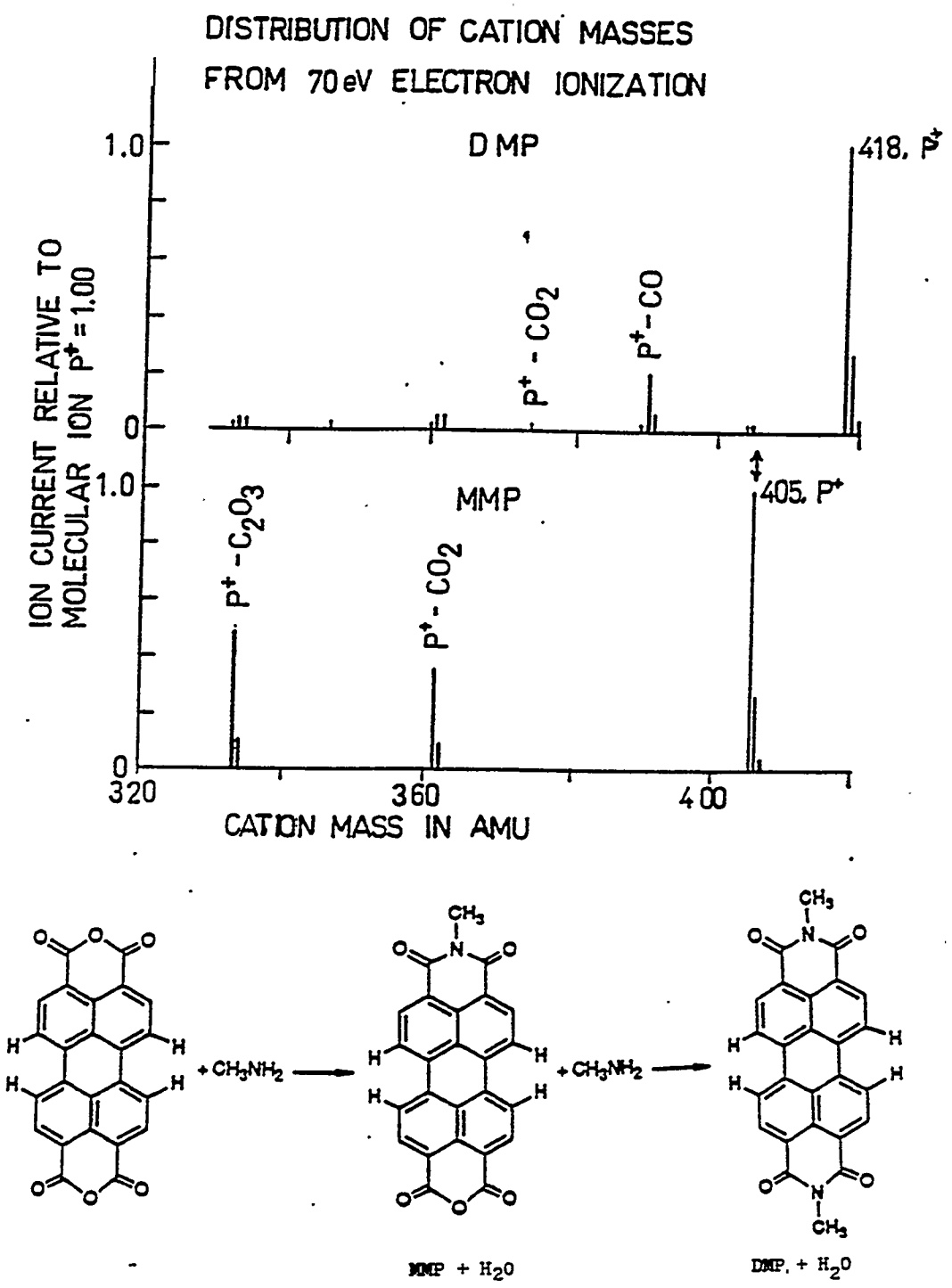


Figure 1. Synthetic scheme for making DMP. The water liberated at each step competes with the methylamine for reaction at the acid anhydride sites, giving a mixture of the desired product DMP on the right with MMP, the monoimide-monoanhydride in the middle. The MMP molecule fits easily into a normal DMP lattice position in the highly insoluble DMP crystal. The mass spectra patterns of DMP above and MMP below show the parent ions of mass 418 and 405 along with weaker peaks for loss of fragments such as CO or CO_2. The DMP pattern from even a relatively good sample shows MMP at a level of roughly 2% of DMP. This shows an intractable impurity, which must be removed by a special process.

under reaction conditions to give the monoimide-monoanhydride MMP, and that this material might be a stubborn impurity, i.e., high melting, insoluble, since it would fit comfortably into a lattice position in the desired product DMP. This is an organic/organic clathrate, and a pervasive difficulty in the perylene materials. It is possible to anticipate impurities of this sort and to form counter-strategies, of which the first part is to find a reliable method of chemical analysis.

The mass spectrum of DMP gives a good example of preferred formation of the parent ion peak, M_o= 418 AMU for $C_{26}H_{14}N_2O_4$ (100%). As is customary, the highest peak is assigned 100% relative intensity. Secondary peaks are seen at 390 AMU (loss of C=O, 20%) and at 374 AMU (loss of CO_2, 2.4%), and the relative stability of DMP is underscored by the absence of 417 AMU (loss of just one proton under 70 eV bombardment).

One has to ask the mass spectroscopist to remove the 1% "noise" threshold that is routinely programmed into many computer-assisted mass spec. instruments. When this is done, a pattern of weak lines is seen in the DMP spectrum at places where no rational loss of atoms or radicals from DMP could produce peaks. This is MMP, as seen in the lower spectrum of a synthetic sample (17). Its parent peak is also the strongest of the set, 405 AMU (100%, for $C_{25}H_{11}NO_5$) and 361 AMU, (2%, loss of CO_2) plus 333 AMU (11% for loss of the entire anhydride function C_2O_3). Loss of anhydride has been observed in mass spectroscopy of other aromatic acid anhydrides. The level of MMP in DMP is on the order of 2-3%, and this has been observed in our own syntheses of DMP and in a commercial sample of "Paliogen Red", Colour Index.

The last painful bit of proof against serial sublimations is a mass spectrum of a relatively good commercial sample of DMP as observed with programmed warming of the sample stage and with computer collection of kinetic data on mass values 418 and 405, shown in Figure 2. Here the time-evolution curves for MMP and DMP are seen to coincide within experimental error. This leads us to assume that MMP is indeed clathrated in DMP, so that little or no purification from one or even three successive train sublimations is to be expected.

As the mass of the perylene derivative rises, mass spectrometry becomes increasingly difficult. There is a simpler alternate method for testing for the intrusion of water appearing in the form of the six-membered ring anhydride of a pair of carboxy acids. This group has very tightly bound anhydride C=O bonds as compared with any other carbonyl group, and is known for its "stand alone" matched pair of IR bands at about 1765 cm^{-1} and 1727 cm^{-1}. In the lowest, coldest band of deposition of an impurity of the bis-1,2-diaminobenzene diadduct to perylene-3,4,9,10-tetracarboxylic acid, we have found a similar pair of IR lines, roughly half as strong as the intrinsic and strongly absorbing band assignable to the carbonyl group or groups adjacent to the benzimidazolo functions on the molecule. This is an invitation to closer scrutiny of future perylene materials, since no other strong lines fall in the region of the anhydride C=O frequencies. This will allow more sensitive analyses on thick pellets of DMP, but the analyses will be unreliable unless done in FTIR instruments with purging of the instrument case by very dry gases to avoid the interference from strong and sharp vibration-rotation lines of the bending vibration of H_2O. An older style double beam IR grating spectrometer with scale expansion can also be used to advantage.

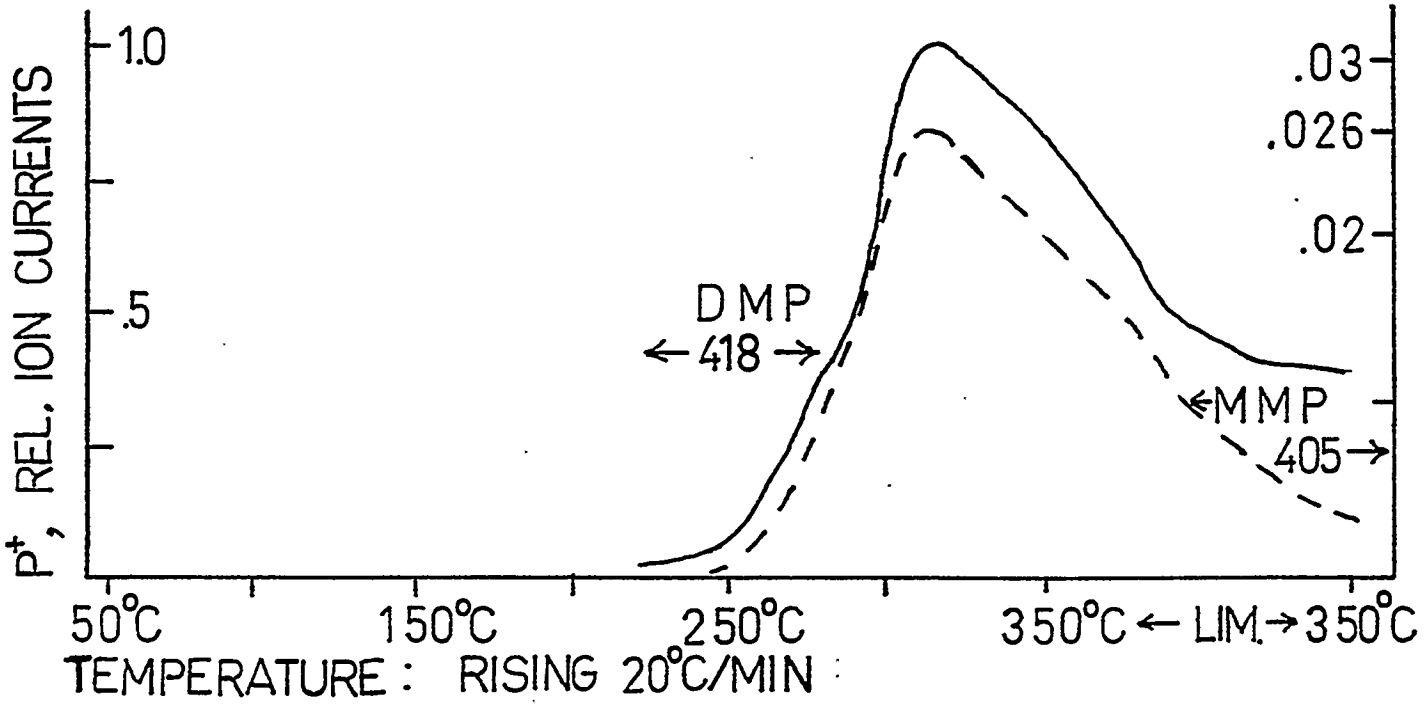


Figure 2. Subliming of a typical DMP sample with MMP in a mass spectrometer. The spectrometer with its computer are programmed to measure DMP and MMP at masses 418 and 405 as the sample is heated. Two substances come off with the same heat/time pattern, Little or no separation is likely by sublimation. which confirms the probable inclusion of MMP in the DMP crystals.

Reactive Train Sublimation

In the case of DMP plus MMP contaminant, the easy way to purify the sample is simply to use the reactant, methylamine as the sweeping gas for train sublimation. We call this "reactive train sublimation (RTS)", and it does bring about partial conversion of pure MMP to DMP on a single pass. It takes advantage of the transient presence and reactivity of the impurity MMP in the gas phase and on the hot surfaces just before and after transportation. The improvement in material tests with Schottky single layer cells and in performance of Phthalocyanine/DMP p-n cells confirms at least partial removal of MMP. The analyses for trace MMP are not now sufficiently sensitive to monitor complete removal. Since a considerable quantity of methylamine is swept through the apparatus, a liquid nitrogen cold trap has to be used and checked frequently for potential stoppage.

This RTS method has some possibility of extension to larger imide substituents. The bis-imide made with aniline could just be swept with aniline vapor in apparatus warmed to about 40C. It's unlikely that any serious thermal reaction of aniline will occur under these condition.

Water, Phthalocyanines, and Phthalocyanine Hydrates

The roles of water as help and hindrance are completely mixed in the best of the phthalocyanine OPV materials, and the knowledge needed to make further improvement has been almost studiously avoided. Titanylphthalocyanine has three readily accessible phases, I, II, and Y, and Chloroaluminum-phthalocyanine has phases I and Y (the ClAlPc phases are tentatively identified by similarity of band shapes and electrophotographic performance to their TiOPc counterparts). The observation that vapors of such "solvents" as methylene chloride, dioxane, or chlorobenzene would "catalyze" formation of the ultimately stable Y-phase in as little as a half hour seemed to us as to others to indicate a phase transition (18). However, with both Pc's, the Y-phase is never present immediately after vacuum evaporation, and the best performance of p-n cells made with these Pc's comes after exposure to air, and especially to water vapor. Fujimaki (19) examined a heating cycle applied to a photoconductive layer of Y-TiOPc microcrystals and found, for an initial relative current of 100 units:

(a.) an initial rise of conductivity to 550 u. @ 90C
(b.) a rapid decline of conductivity to 120 u. after continued heating to 140C. We now associate the drop in conductivity to loss of water from the Y-phase.
(c.) a catastrophic drop to 2.1 u. conductivity while the sample cooled back to starting T.
(d.) recovery to 50 u. of current on exposure to oxygen-free water vapor. Further O_2 recovery not tested.

We can now understand this cycle as involving the polycrystalline Y-phase sample, previously made by vapor exposure of amorphous TiOPc to make the water-stabilized phase TiOPc·H_2O, followed by water removal at *ca.* 105-115C. Shortly after the "adsorption" to TiOPc became known, we recognized the role of water in ClAlPc, and showed that the "phase transition" could go forward over air of controlled humidity as low as 40% (12). We found that it involved the uptake of two

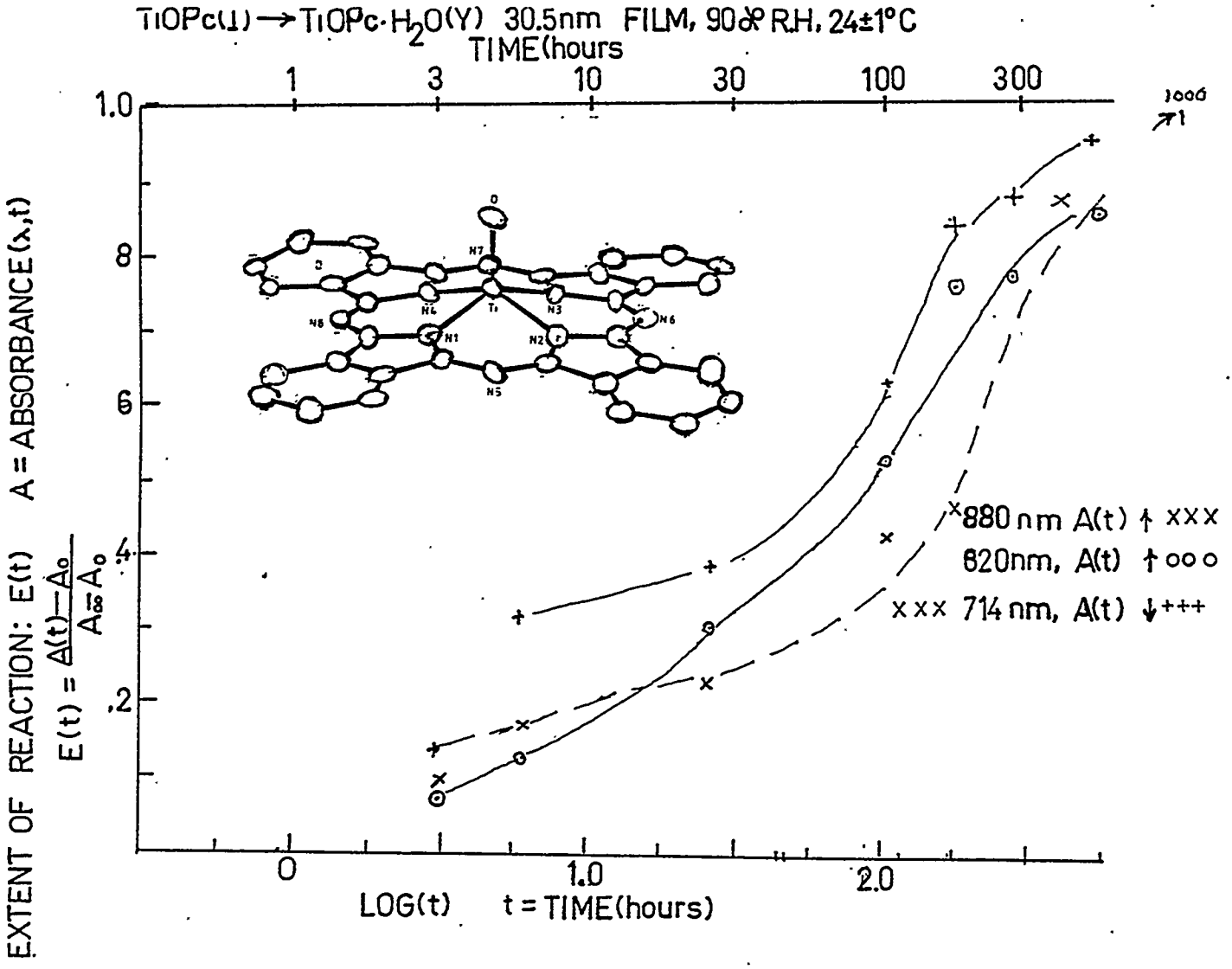


Figure 3. Interplay of three different crystal structures of Titanylphthalocyanine. Each has a characteristic color as may be seen in a thin film sample such as this 30.5 nm evaporated film on glass. The original film had a strong absorption band at 714 nm peak, structure I. Over 1000 hours, the 714 nm absorption disappeared, and the 820 nm absorption (phase II) and the 880 nm absorption (phase Y) dominate. The 880 nm absorber (phase Y) is formed by adding water to either I or II by exposure of the film to 90% relative humidity at room temperature. The Y-Phase is far more sensitive to light and will give the most electrical power of the three. Dry air or heating can slowly dry Y and cut power generation.

molecules of water per molecule of Pc, and proposed a hydrogen-bonding structure which can account for uptake of one mole H_2O per mole of Pc. The slow optical conversion of an evaporated layer of TiOPc(I, II) under 90% relative humidity is shown in Figure 3. The wet phases of the two metal Pc's are remarkably similar in rate of hydration, but TGA studies show a loss of water from ClAlPc·$2H_2O$ at a considerably higher temperature of about 130C with a suggestion of differentiation between the rates of evolution of the successive water molecules. In both metal Pc series, the hydrates have the best crystal photoconductivity and the best structure for long range exciton propagation. The word "adsorption" for TiOPc·H_2O may have been an unfortunate logical impediment. Adsorption implies disordered multi-site attachment. Hydrates, on the other hand, are commonly considered to have ordered molecular structures, and with these precise points of attachment, as we believe, in the hydrated crystal structure.

Formation and Handling of the Phthalocyanine Hydrates

All of the workers familiar with handling these compounds have expressed a sense that the water is not just a geometric adjustment, but that it also assists in charge separation. After the water of crystallization is removed, the TiOPc molecules remain in metastable position in what is best called the "Dry-Y" phase. If the material is not heated to 260C, this phase persists and relatively rapidly adsorbs ambient water to regenerate the fully hydrated Y-TiOPc·H_2O. We do not, at this moment, know the lowest relative humidity at which the Y-phases are stable at room temperature. In the interest of doing feasibility trials on these remarkably efficient Pc-hydrates, the phase diagrams of the materials need to be explored with respect to water at and above ambient conditions. However, our optical observations on phase conversion of evaporated layers *ca.* 30 nm in thickness indicate that times up to 1000 hours are needed at room temperature for hydration and reorganization to complete the spectral shifts associated with the Y-phase. At the other extreme, the complete hydration of ClAlPc in a few minutes of contact with cold water- accidentally applied- has been observed with an evaporated layer deposited on a glass substrate at -127C in order to make a truly microcrystalline layer. Vacuum was broken prematurely, and water froze, melted, and quickly evaporated from the film. Maximum surface area favors rapid addition of water, as does disorder in the crystallites. Any useful study of phase relationships in these two hydrates will have to extend to TEM and crystallographic evaluations of changes in particle size and film integrity. The lack of any reference to prolonged holding times to restore water content in Fujimaki's work suggests to us that the exposed "dry Y" phase returns to Y-TiOPc·H_2O in a matter of a few days or less, much faster than the original hydration.

The need for controlled experiment has to be stressed. In the case of these hydrated phases, the only precise way to control an experiment in photoconductivity or photovoltaic action is to keep the sample in vapor contact with a source of water vapor at controlled partial pressure. This may be easily done with a humidistat, such as an open beaker containing saturated NaCl solution plus solid NaCl. This is a favored system which maintains 75% relative humidity over a wide range of temperatures. The corresponding KCl system gives 85% humidity. Note here that KBr forms a stable dihydrate KBr ·$2H_2O$, and that this excess of water may be carried into later stages of

investigation, especially if KBr discs are used to collect IR spectra. KCl is a bit more brittle, but tends to give more normal pellets for IR of hydrated materials.

We have been deeply dissatisfied over the Rietveld analysis of Y-TiOPc published by Oka, Okada, and Nukada, since they made no effort to locate the oxygen (water) atoms in the crystal structure (20). If they sought and analyzed a "dry Y" dehydrated Y-TiOPc, it should have been so identified. There is a pressing need to know the binding site(s) of water in crystal structures of the Y-compounds, held at full hydration for the determination. We have not abandoned hope of growing fully hydrated diffraction-grade crystals of Y-TiOPc and Y-ClAlPc. In fact, it is especially important to do so, as these compounds are the best p-type materials on hand with a broad base of experience to use in a feasibility experiment under controlled humidity to prevent water loss. The formation of films of these compounds in the Y-phase is tedious but not impossible, and the phase diagrams at elevated temperatures may open faster and easier routes to workable films.

Bis-Benzimidazole Perylene (alias BZP, BBIP etc.)

This pair of compounds (cis and trans) give so much promise of even better charge-separation behavior (11, 21.) and such unique problems to delay improvement that we consider them apart from the more familiar perylene derivatives. The cis- and trans-isomers of the dehydrated 2x adduct of 1,2-diaminobenzene with perylene 3,4; 9,10-dianhydride, has excited great interest as one of the most sensitive members of the high quantum yield-low field photoconductors. The synthesis has long been understood to produce an uncontrolled mixture of the cis- and trans-adducts. A careful study of the NMR spectra of sulfur adducts to this pair of compounds was made at the Xerox of Canada Laboratories by Duff, Hamer, and Hor (22) and proved the presence of the two isomers. Chemical Abstracts has assigned separate CAS numbers to the two isomers (55-034-81-6 and 55-034-79-2). However, we are not aware of any attempt to separate these isomers, nor has any convenient analytical method of following a separation process been offered. We find this situation illogical in the case of such a promising OPV material. Our hypotheses are:

1. Either separated isomer of BBIP would be superior to the present uncontrolled mixture for OPC or electrophotographic applications and certainly for OPV use.
2. This mixture is already an independent proof that we do not need to tolerate environmentally sensitive hydrates for superior OPV work.
3. Either of these separated isomers may be the best available n-type OPC for the critical test of organic solar cells.

On February 5th, 1996, we presented to the Department of Energy/Basic Energy Sciences Division Workshop at Estes Park, Colorado our new results on BBIP, including Prof. Emge's then-partially successful crystal structure determination and the writer's optical observation that some fractionation of the isomers occurs in train sublimation. This seems to have enabled the selection of isolated crystals of diffraction-grade BBIP, which gave over 1900 diffraction spots above 2σ but also showed a disorder which might at first have been either a cis-trans mixture or a 2-fold rotation of individual trans-BBIP molecules about their long axes in the crystals. In the last day before submission of this

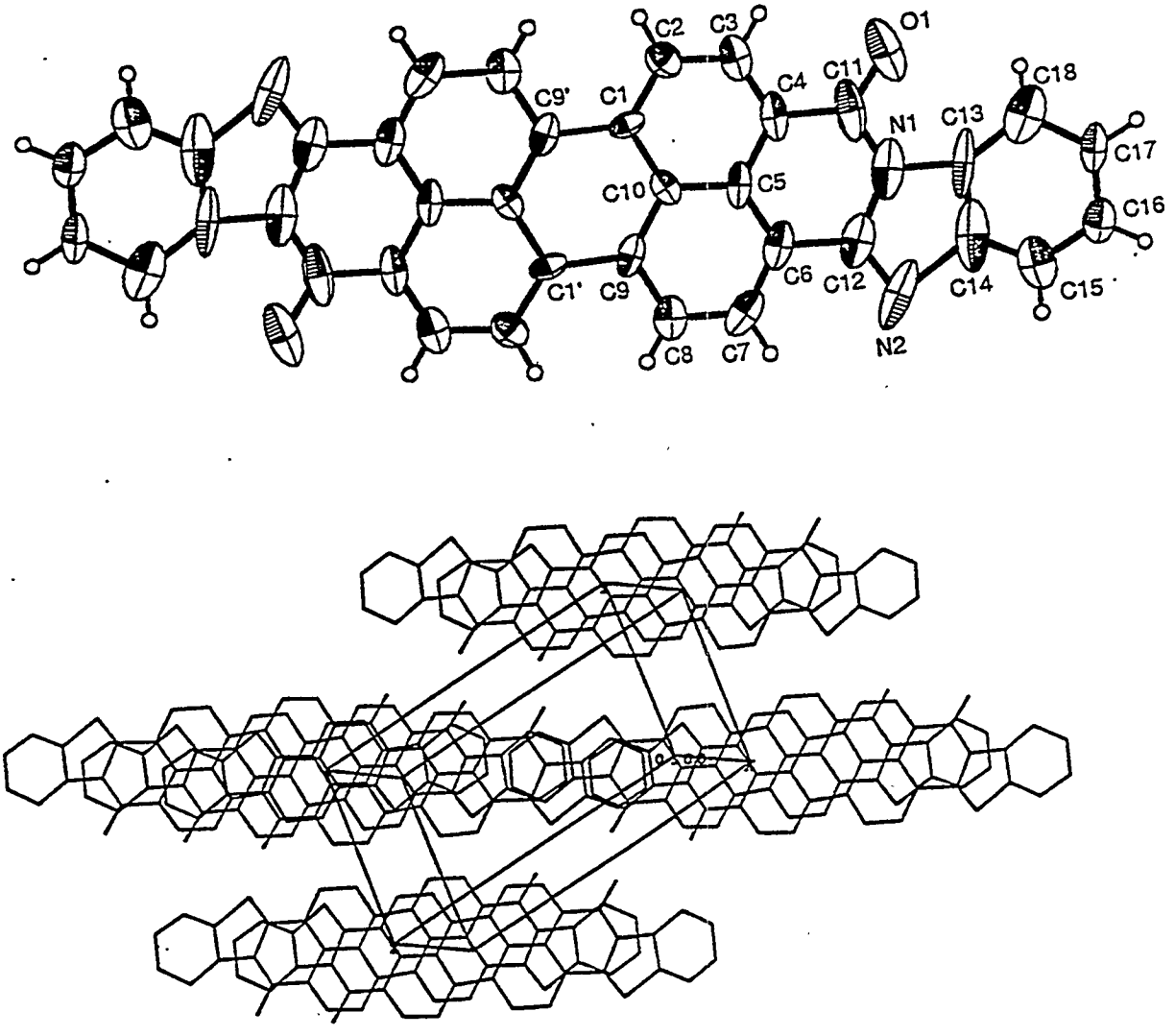


Figure 4. X-ray structure of Bis-Benzimidazole Perylene (BBIP or BZP). This material is actually a mixture of cis and trans isomers, but single crystals deposited at very high temperatures are now found to consist of the trans form. You can recognize trans molecules by the oxygens which are projecting outwards on opposite sides of each molecule. This work is directed toward obtaining the separate isomers either of which might be a considerable better photovoltaic material than the material now used.

Figure 4. Appendix. X-ray structure determination details.

Crystal data and structure refinement for BBIP

Empirical formula	C36 H16 N4 O2
Formula weight	536.52
Temperature	293(2) K
Crystal system	Triclinic
Space group	P-1, #2
No., θ range for cell det'n	25 reflections, 10.2 to 21.5 °
Unit cell dimensions	a = 4.734(2) Å α = 86.12(3) ° b = 8.767(3) Å β = 99.44(3) ° c = 14.274(5) Å γ = 81.65(3) °
Volume	575.7(4) Å^3
Z	1
Density (calculated)	1.548 Mg/m^3
Absorption coefficient	0.790 mm^{-1}
F(000)	276
Crystal color, description	v. dark green-blue, swords
Crystal size	0.40 x 0.10 x 0.03 mm
θ range for data collection	2 to 65 °
Index ranges	-5<=h<=5, -10<=k<=10, -16<=l<=16
Reflections collected	3627
Independent reflections	1913 [R(int) = 0.0243]
Observed reflections	1281
Max. and min. transmission	0.779 and 0.722
Refinement method	Full-matrix least-squares on F^2
Data / parameters	1909 / 190
Goodness-of-fit on F^2	1.006
Final R(F), wR(F^2) [I>2σ(I)]	0.145, 0.341
Final R(F), wR(F^2) [all data]	0.186, 0.382
Largest diff. peak and hole	0.4 and -0.4 e·Å^{-3}

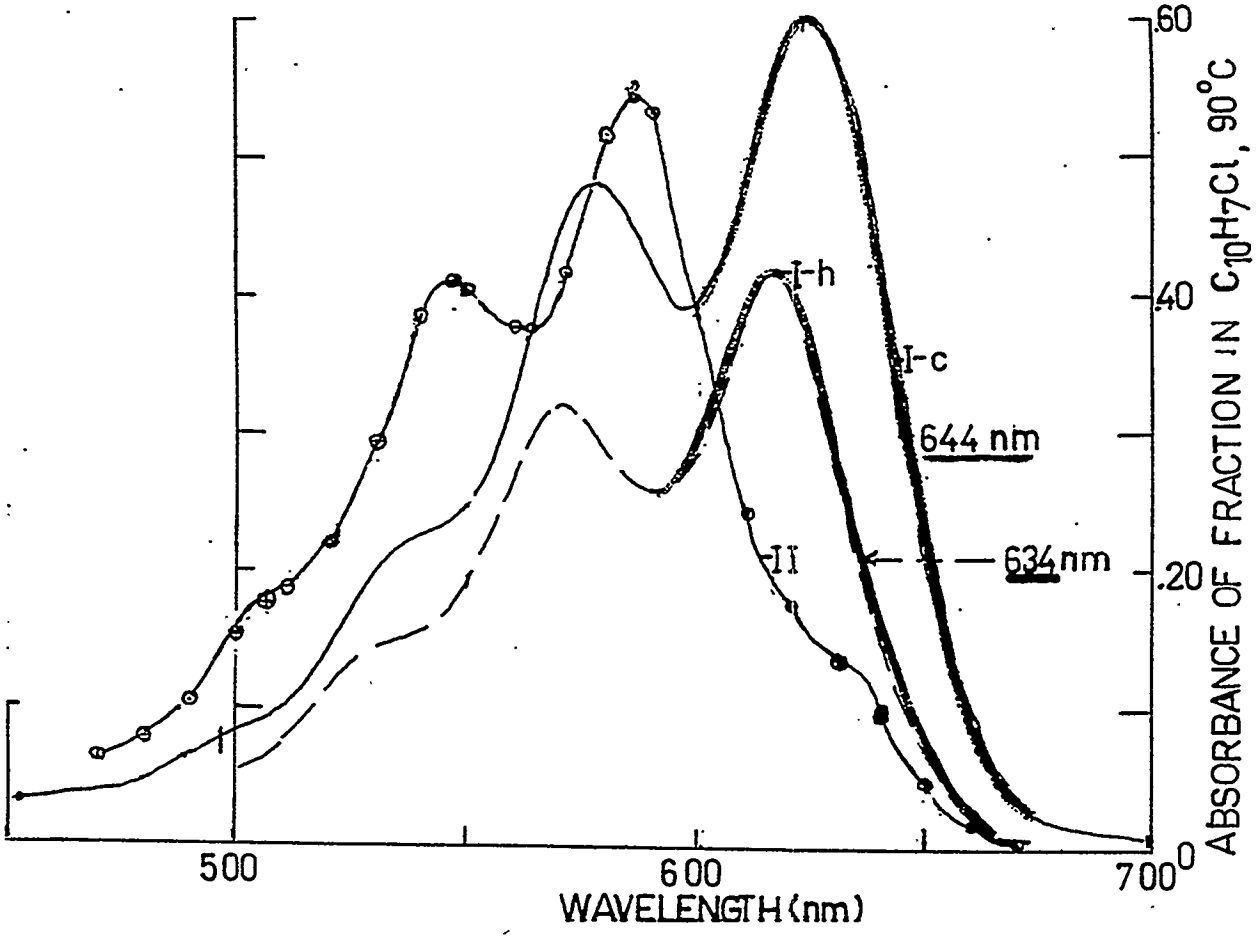


Figure 5. A simple analysis of BBIP mixtures by visible absorption in hot (90C) 1-chloronaphthalene. The cis and trans absorptions were expected to be similar, but the two fractions taken at hot (I-h) and cooler furnace zones (I-c) show half-peak absorptions of 634 nm (hot) and 644 nm (cool), presumably trans and cis enriched, respectively. The separate cold band II gives an impurity resembling MMP and showing an infrared anhydride band.

manuscript, the analysis of the disorder in the crystal has now been fully interpreted. The structure of molecules in the crystals is the trans form, as may be seen in Figure 4. The crystal data with details of refinement follow as an Appendix. This is most easily seen by noting the projecting sticks or single atoms, which are the oxygens and define the structure. The disorder is still there, but is proved to involve only a slight rotation of whole molecules which remain in their proper plane. The immediate result from this analysis is that powder patterns have been calculated from this single crystal result, and these pattern fit data going back more than ten years. We have every hope that this work will illuminate both past and future. The preliminary analysis of enrichment by visible spectroscopy of hot solutions will be a more pedestrian help in developing enrichment procedures. Spectra are given in Figure 5. The stage is now set to refine this material for inclusion as a particularly choice OPV material for feasibility testing in p-n diodes with favored phthalocyanines.

Summary

By separating interim goals we have been able to define an experimental track to bring out the best in existing high stability Organic Photoconductors which have been identified in electrophotographic research as having high quantum yields of separated charge carriers at fields considered low in the EP industry. Strangely, these materials have not been pushed beyond immediate industry goals to an analysis sufficiently stringent to predict solar photovoltaic performance. A choice of two or three candidate pairs of p- and n-dyes with high quantum yields of charge carriers and high fill factors is to be expected after a limited period of undiverted work. One can also have strategies at hand to make final adjustments that might be needed after the initial major cycle of improvement.

Acknowledgements

Having been asked to stand and speak for a recently neglected and promising field of energy research, the writer offers his deepest thanks to Rutgers friends young and old who shared the quiet struggle to keep this field alive and lent joy to it along the way. Their names and contributions adorn this text and bibliography.

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LIGHT-INDUCED METASTABLE STRUCTURAL CHANGES IN HYDROGENATED AMORPHOUS SILICON

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Abstract

Light-induced defects (LID) in hydrogenated amorphous silicon (a-Si:H) and its alloys limit the ultimate efficiency of solar panels made with these materials. This paper reviews a variety of attempts to find the origin of and to eliminate the processes that give rise to LIDs. These attempts include novel deposition processes and the reduction of impurities. Material improvements achieved over the past decade are associated more with the material's microstructure than with eliminating LIDs. We conclude that metastable LIDs are a natural by-product of structural changes which are generally associated with non-radiative electron-hole recombination in amorphous semiconductors.

Introduction

The greatest problem facing amorphous semiconductor photovoltaics is photodegradation of a-Si:H and its alloys (1,2). The defects produced by light exposure, LIDs, are three-fold coordinated Si atoms which act as efficient recombination centers. Without photodegradation one can produce solar panels with conversion efficiencies near 15% instead of the 10-11% efficiency after degradation (3) Many improvements in solar cell design and performance have been achieved over the past decade. The improvements result less from a reduction in photodegradation than from an improvement in minority carrier lifetime due to greater homogeneity and less microstructure found in the present material. In the following we explore to what degree photodegradation is linked to material processing and hence to microstructure or to impurities. We then discuss experiments which show that photo-degradation produces not only LIDs but other structural changes.

Microstructure

Knights (4) showed that microscopically visible columnar growth structures appear in the parameter regime of physical vapor deposition at high deposition rates or when energetic ions bombard the growth surface. High quality films are obtained in the chemical vapor deposition regime at low rates. Even then the films are not homogeneous, the 8-10 atom percent hydrogen is bonded as dilute Si-H bonds and in regions of clustered hydrides (5). Moreover, the hydrogen can be bonded as silicon-monohydride or a di- and polyhydride according to infrared absorption spectra. The clustered hydride phase is probably located at the internal surfaces of microvoids. Williamson (6) determined the size, shape and volume fraction of these voids by small-angle X-ray scattering. Void volume fractions typically range from 0.1% in good films to 1 or 2% in Si-Ge or Si-C alloys or films deposited at high rates with void sizes between 1-8nm.

Figure 1 shows a sketch of microstructure features envisioned in relatively good a-Si:H material. In alloys one may expect in addition clustering of the constituent atoms, Si and Ge or Si and C. Figure 2 shows some low-angle x-ray scattering results of Williamson and the increase in scattering and void fraction with Ge alloying.

Improved material quality was obtained by hydrogen dilution of the silane or disilane feed gas. The additional hydrogen in the plasma is believed to promote the removal of weak Si bonds during the growth process. The hydrogen concentration in the film, about 8-10 atomic percent is thereby not affected. Figure 1 shows that low-angle x-ray diffraction fails to detect the effect of H-dilution of the plasma gas. However, differences in microstructure and hydrogen bonding are revealed by infrared absorption and hydrogen evolution spectra (7). An example of the latter is shown in Figure 3. The samples use here are further described in Table I. Hydrogen evolution occurs at different temperatures indicating different energies of hydrogen release and subsequent bond reconstruction. In some cases hydrogen effusion is facilitated by an interconnected void structure (8).

We next explore whether the creation of LIDs is linked to faults in the material's structure which could possibly be removed by better deposition techniques.

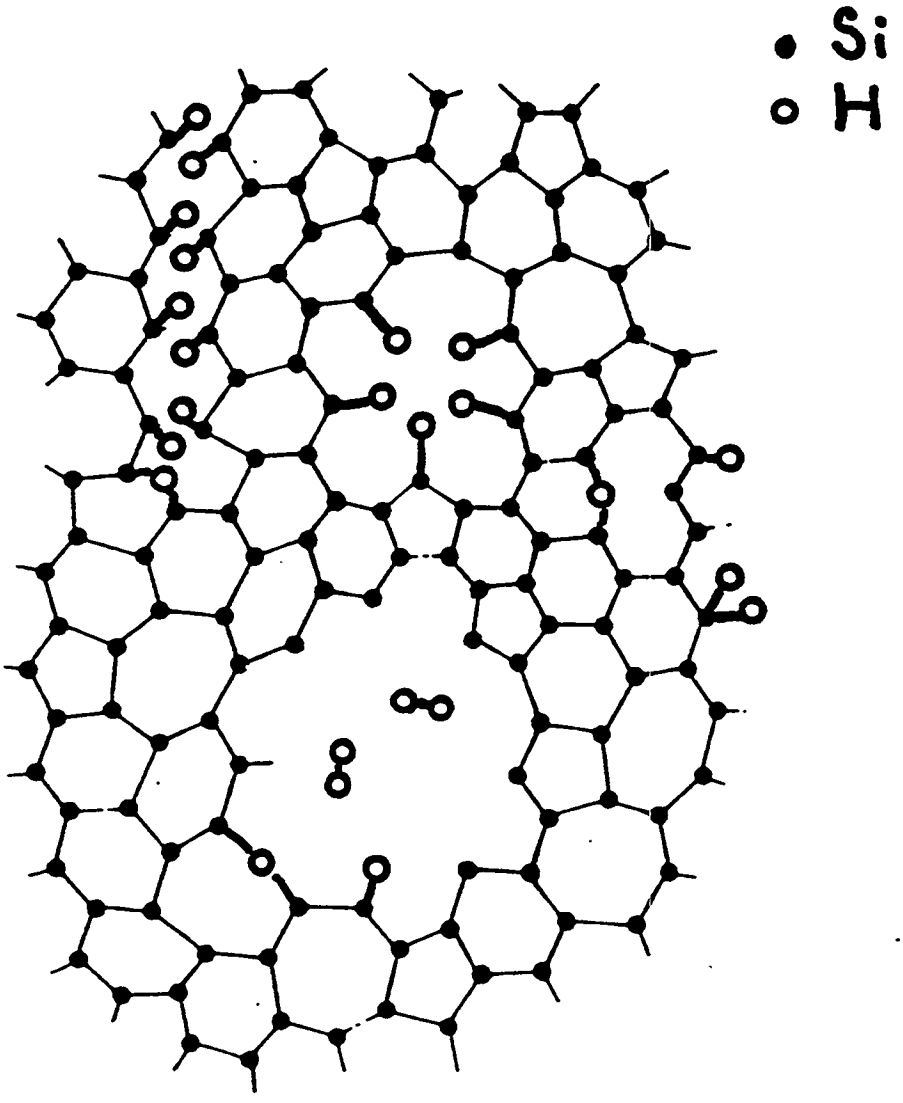
Table I Characteristics of USSC samples

Sample No.	type	T_s(°C)	H_2 dilution	E_{opt} (eV)	C_H(%)	N_D(o)(cm^{-3})	N_D(1000h)(cm^{-3})
1 - 6403	a-Si:H	300	low	1.72	8.1	2.9E15	2.9E16
2 - 6407	a-Si:H	300	high	1.74	7.4	4.4E15	3.0E16
3 - 6405A	a-Si:H	175	low	1.77	13.2	5.0E15	2.5E16
4 - 6405B	a-Si:H	175	high	1.79	12.3	7.9E15	3.0E16
5 - 6419	a-SiGe:H	300	low	1.40	6.4	6.4E15	
6 - 6411	a-SiGe:H	300	high	1.43		4.0E15	

Table II Sample Characteristics

		T (°C)	Rate (Å/s)	C_H (%)	E_o (eV)	N_D(cm^{-3}) annealed	N_D(cm^{-3}) t_{ex}=120h
GD1	Chicago	230	1	8	1.75	$5x10^{15}$	$5x10^{16}$
GD2	Chicago	230	1	8	1.72	$1x10^{16}$	
HM	ETL	250	0.5	9.8	1.75	$3x10^{15}$	$5x10^{16}$
HW	NREL	> 400	5 - 10	1.7	1.7	$1x10^{16}$	$4x10^{16}$
RP	Xerox	400		10	1.75	$7x10^{15}$	$4x10^{16}$

Fig. 1. Schematic of possible microstructural features in hydrogenated amorphous silicon



also possible:
Ge or C clustering or segregation
microcrystal formation

Figure 1. Sketch of microstructure feature sin a-Si:H (after Williamson)

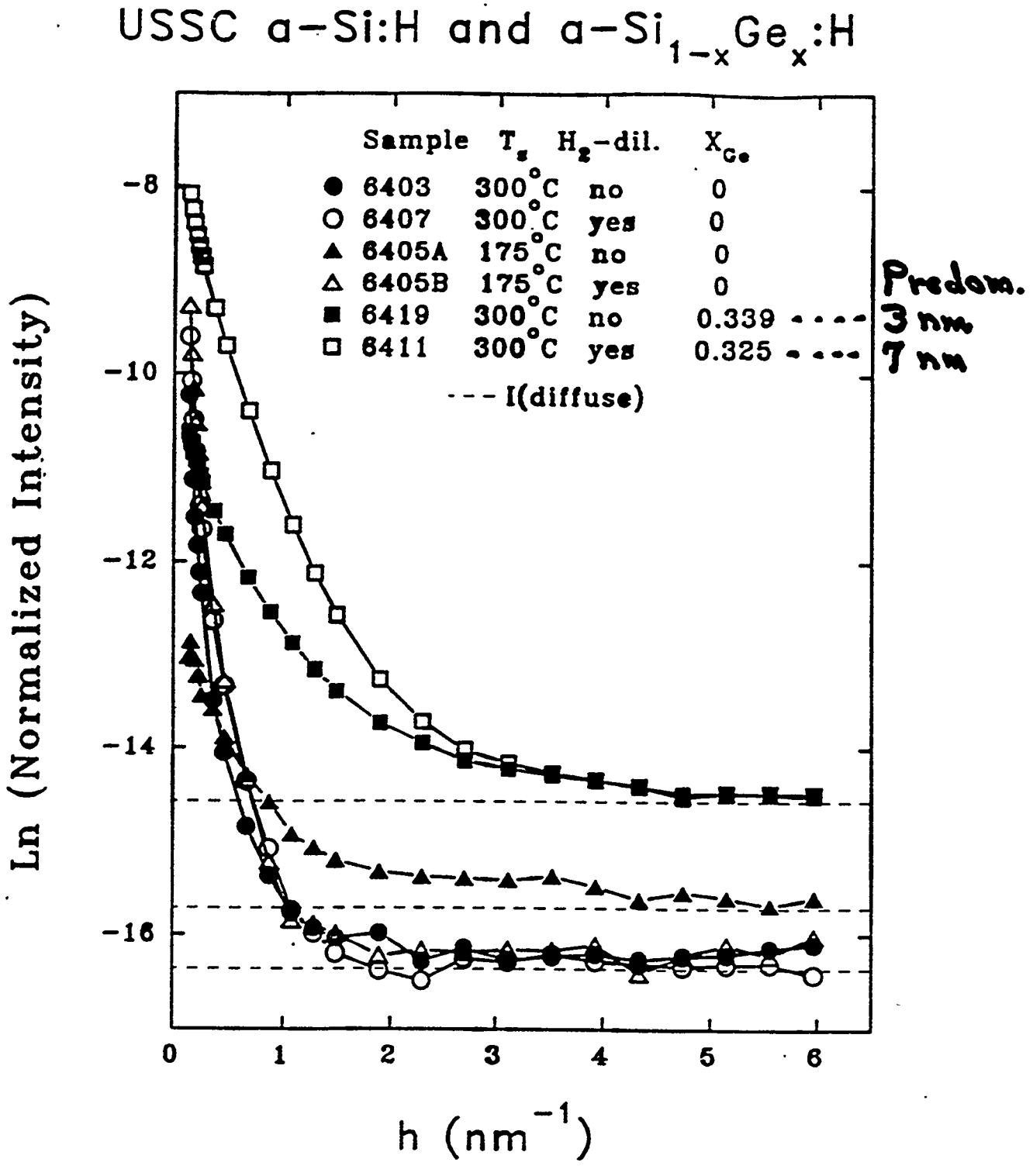


Figure 2. Small-angle x-ray scattering data of a-Si:H and a-$Si_{1-x}Ge_x$:H prepared with and without hydrogen dilution at different substrate temperatures T_s. Samples are described in Table I. h=4psinQ/l where l=0.154nm and 2Q is the scattering angle. See Williamson, ref. 6.

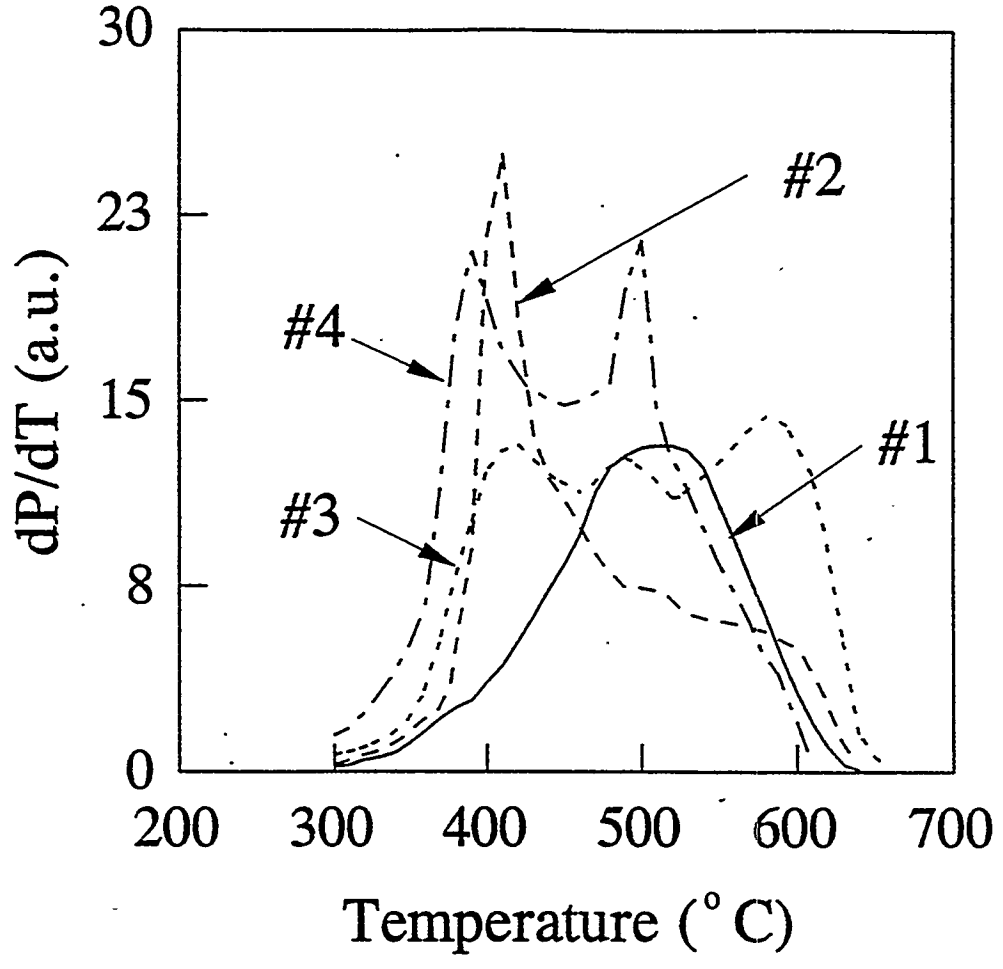


Figure 3. Hydrogen evolution spectra of a-Si:H samples described in Table I.

Dependence of Photodegradation on Preparation Method

Considerable effort has been devoted to improving the material quality by changing the deposition conditions. Among these are hydrogen or helium dilution of the plasma gas, the use of Si_2H_6 instead of SiH_4, higher frequency than the conventional 13.6 MHZ, remote plasma (RP) which reduces ion bombardment of the growth surface (9), heated mesh (HM) which promotes surface mobility of the SiH_2 precursors (10), hot wire (HW) deposition which allows the growth of a-Si:H that contains only a small fraction of the hydrogen concentration of conventional material (11), and alternating film growth with hydrogen plasma etching which is called chemical annealing (12).

We subjected samples prepared by four different techniques to the same light exposures and measured the increase in LIDs by the constant photocurrent method (CPM) as well as the degradation of the photoconductivity between 4.2 and 300K (13). Table II shows the sample characteristics before and after a 120h exposure to an electron-hole pair generation rate of G = $1.1x10^{22}cm^{-3}s^{-1}$. Two samples GD1 and GD2 prepared in Chicago by conventional plasma assisted chemical vapor deposition without hydrogen dilution are among the samples studied. Figures 4, 5 and 6 show the photoconductivities measured with a photon flux of $2x10^{14}cm^{-2}s^{-1}$ of the annealed state and after a 1h exposure to G = $3.7x10^{21}cm^{-3}s^{-1}$ and a 120h exposure to G = $1.1x10^{22}cm^{-3}s^{-1}$, respectively. The sample qualities of the samples are quite different in the annealed state but practically the same after extended light exposure. The hot wire sample used here was prepared in the same deposition run which produced a sample which was reported to show negligible photodegradation (14). The results shown here have the advantage that the test conditions were the same for all samples.

We conclude that greatly different preparation techniques which are likely to yield films with different microstructure, have little or no effect on photodegradation. Their effect on minority carrier lifetime and other parameters affecting solar cell efficiencies cannot be tested by measuring CPM and photoconductivity.

Impurities

Oxygen, carbon, and nitrogen are common impurities in a-Si:H and its alloys. In most cases the impurity concentration is larger than $N_D=2x10^{17}cm^{-3}$, the maximum concentration of LID's produced by steady light (15). Even though early work showed no relation between photodegradation and the concentrations of these impurities (16) one felt that definite proof required material whose impurity concentration is less than N_D. I understand that this has finally been done and that photodegradation cannot be eliminated by improving the material's purity (17).

Light-Induced Structural Changes

The principal manifestation of photodegradation of a-Si:H and its alloys is the appearance of LIDs which are silicon dangling bonds which have states near the middle of the gap and thus act as efficient recombination centers. They are easily detectable by electron spin resonance and by an

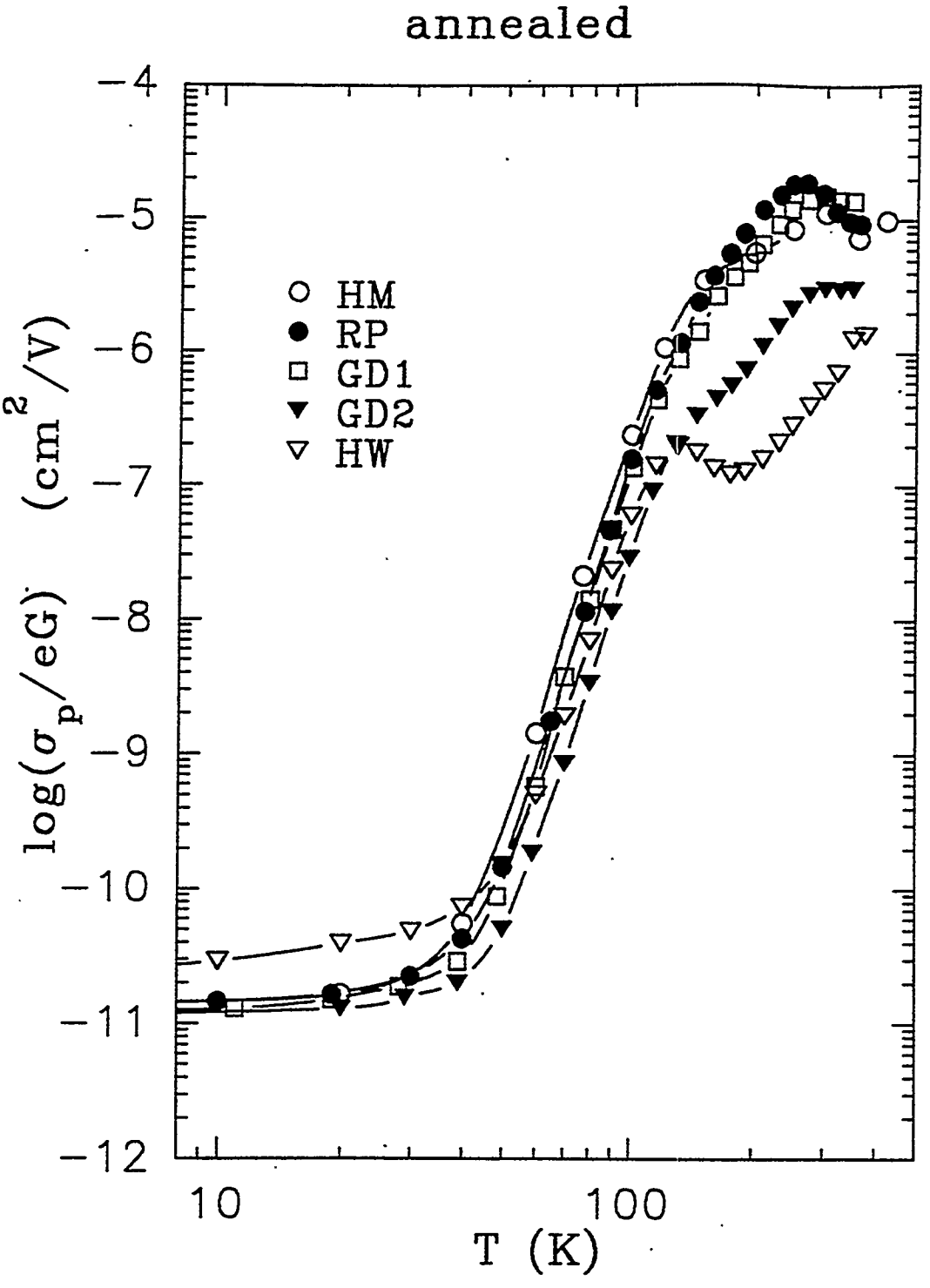


Figure 4. Temperature dependence of photoconductivity s_p normalized by electron charge e and generation rate G of annealed samples described in Table II.

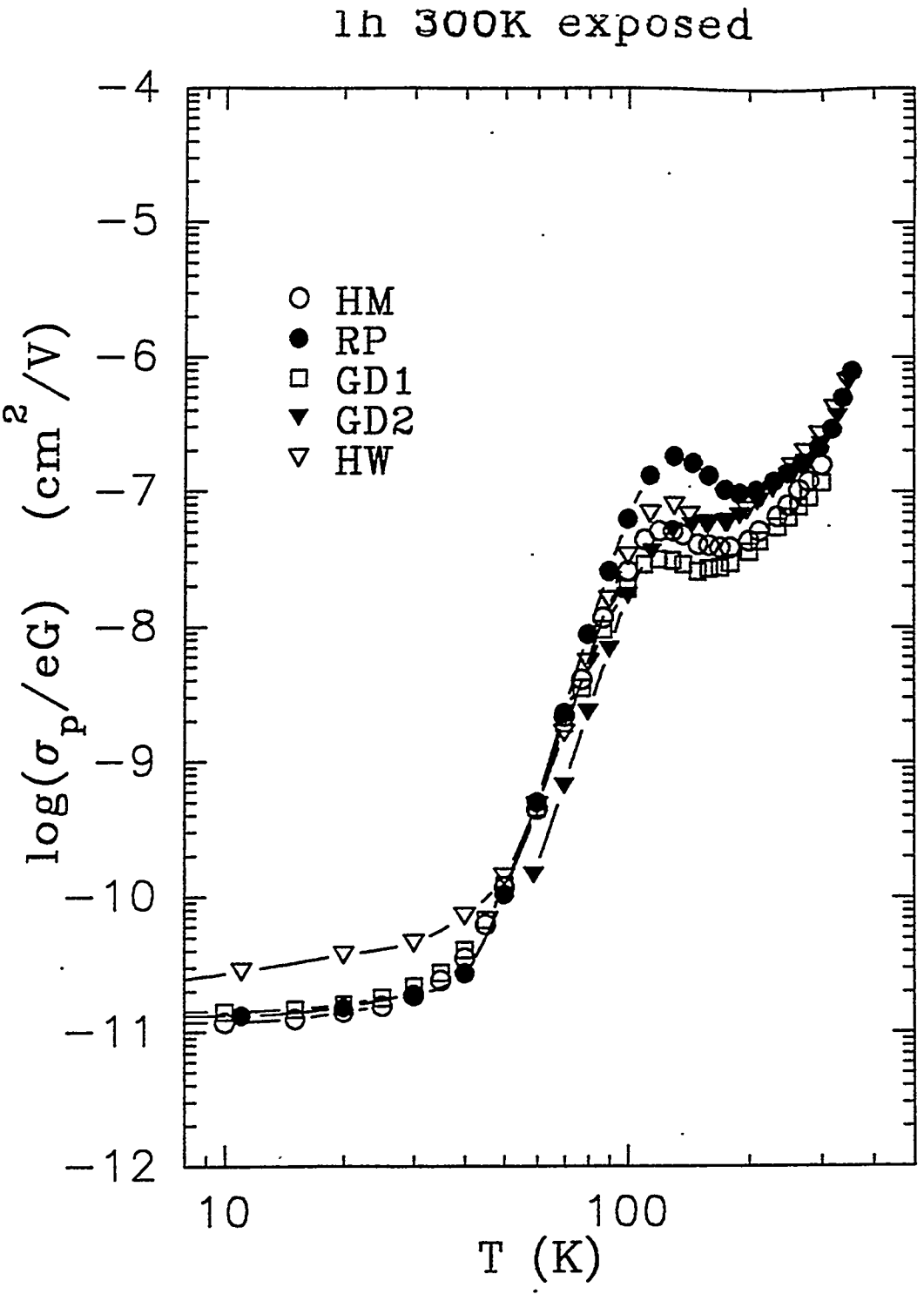


Figure 5. Same as Figure 4 after 1h exposure to G=3.7x10^{21}cm^{-3}s^{-1}.

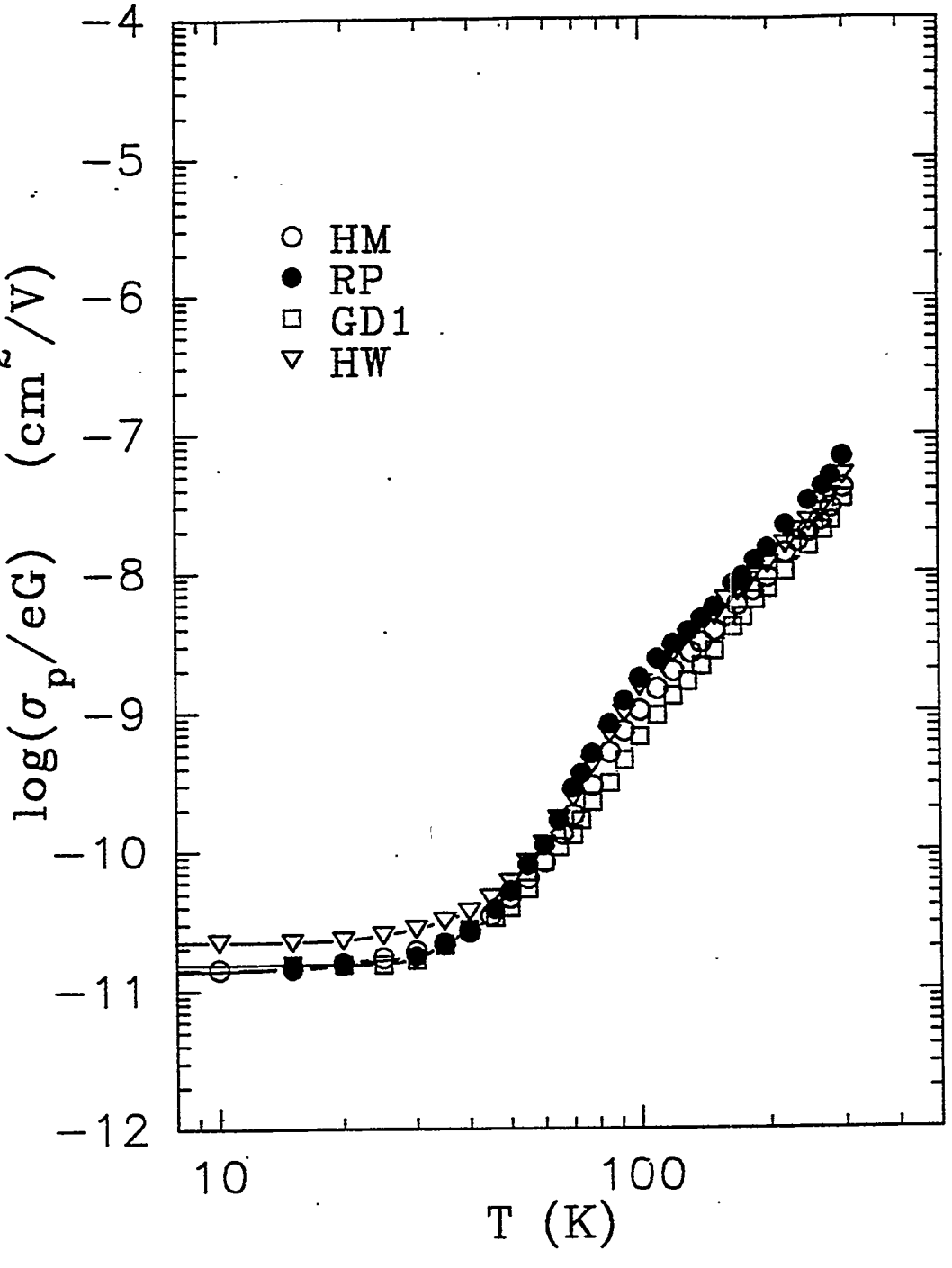


Figure 6. Same as Figure 4 after 120h exposure to $G=1.1\times10^{22}cm^{-3}s^{-1}$.

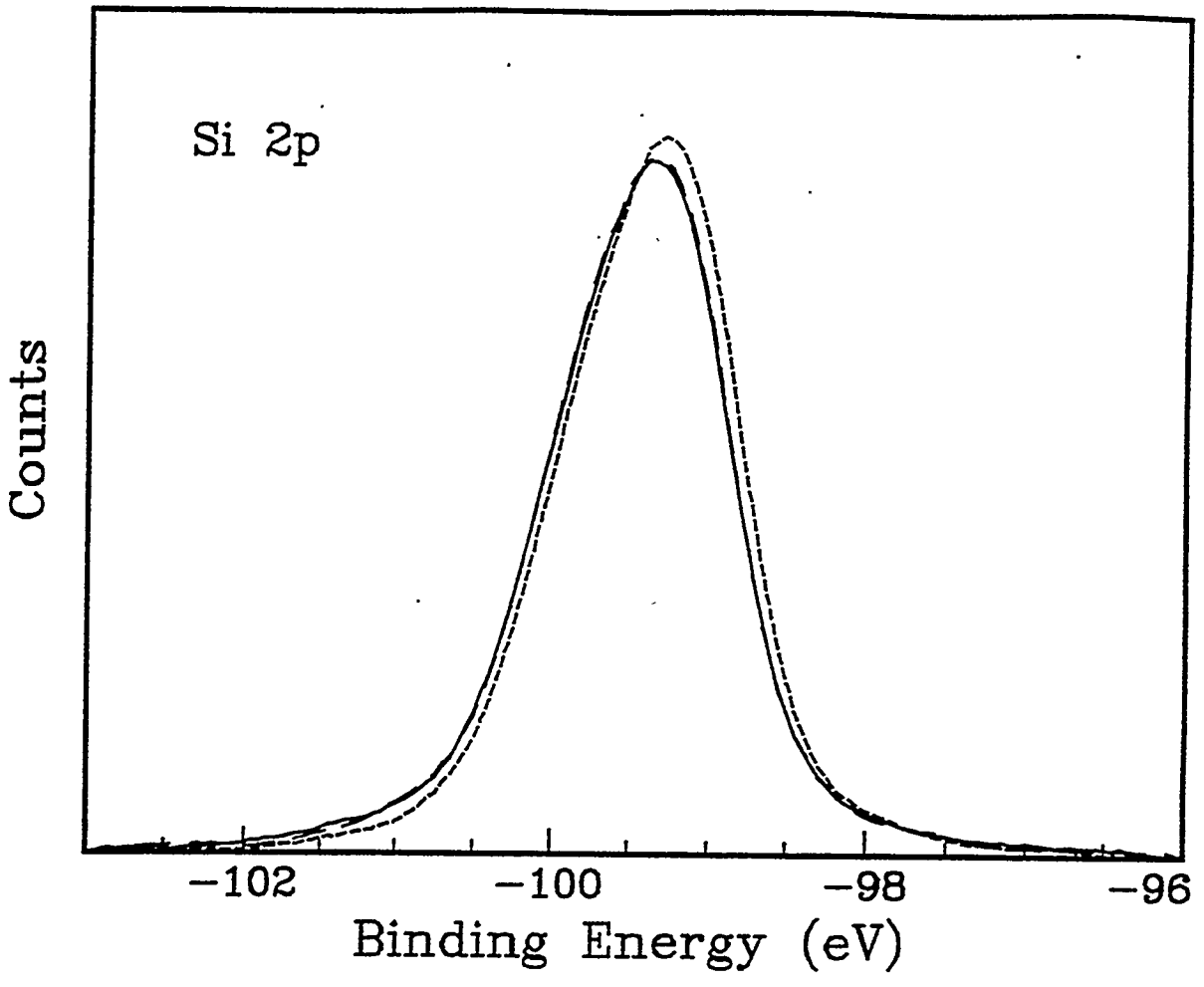


Figure 7. Shift of Si 2p photoelectron spectroscopy peak in a-Si:H due to 24h exposure to 100mWcm-2 white light. The dotted line is shifted by about 0.1 eV to lower binding energy after light soaking. After Masson et al.[22].

increased optical absorption associated with excitations between these defect states and either the valence or the conduction band.

The question arises whether the LIDs are the only consequence of photodegradation or whether there are further structural changes. If the former is true then the photo-induced changes of all properties must be uniquely related to the LID concentration (18). This has not been found to be the case (19,20). For example, the relation between changes in photoconductivity and LID concentration is not single-valued. The relation is different for defect creation and defect annealing and also different for degradations at different temperatures and with steady light and laser pulses (21).

Furthermore, recent experiments revealed a reversible light-induced shift (22) of the Si 2p photoelectron spectroscopy peak, shown in Figure 7, and a light-induced reversible increase (23) in the Si-H stretching mode at wave number =2000cm^{-1}. Moreover, changes in the proton NMR dipolar spin lattice relaxation time were observed to result from light exposure of a-Si:H (24). These changes are much too large to be caused by the relatively small concentration (~10^{17}cm^{-3}) of LIDs. These observations suggest that light exposures not only produce LIDs but also structural changes that involve the majority of the constituent atoms (25). It is too early to tell but the LIDs might be a by-product, albeit a very noticeable one, of structural changes that occur as a result of non-radiative recombinations which deposit an energy of about 1-1.3eV in a relatively small recombination volume (25). Photo-induced structural changes accompanied by a metastable increase in native defects are generally observed in other amorphous semiconductors, for example, in chalcogenide glasses (26,27). In these materials the photostructural changes are much easier to observe than the increase in defect density because the defects are diamagnetic and the structural changes produce photodarkening, which is a red-shift of the absorption edge.

Conclusions

Present evidence suggests that photo-degradation of a-Si:H and its alloys is germane to the material. The magnitude of degradation may depend to some degree on the material quality or microstructure but these variations are small and fail to point the way for eliminating the problem.

Acknowledgements

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PROGRESS IN MOLECULAR PRECURSORS FOR ELECTRONIC MATERIALS

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Abstract

Molecular-precursor chemistry provides an essential underpinning to all electronic-materials technologies, including photovoltaics and related areas of direct interest to the DOE. Materials synthesis and processing is a rapidly developing field in which advances in molecular precursors are playing a major role. This article surveys selected recent research examples that define the exciting current directions in molecular-precursor science. These directions include growth of increasingly complex structures and stoichiometries, surface-selective growth, kinetic growth of metastable materials, growth of size-controlled quantum dots and quantum-dot arrays, and growth at progressively lower temperatures. Continued progress in molecular-precursor chemistry will afford precise control over the crystal structures, nanostructures, and microstructures of electronic materials.

Introduction

The chemistry of materials synthesis and processing is undergoing revolutionary development. Routine synthetic control over the crystal structures, nanostructures, and microstructures in integrated materials architectures will be achieved in the not-too-distant future (1,2). When looked back upon, the present stage of materials chemistry will likely be compared to the emergence of synthetic organic chemistry a century ago. That emergence was strongly tied to developments in dyes, polymers, and pharmaceuticals that remain a significant core of the chemical industry today. We may optimistically project that materials chemistry will be as important to the industries and technologies of tomorrow. Much of the recent progress has been built upon molecular precursors and their reaction chemistry. This chemistry is vitally important to DOE goals.

DOE interest in molecular-precursor chemistry derives from the component materials, fabrication issues, and environmental and safety considerations associated with current research in photovoltaic (PV) devices. PV-cell designs require coassembly of metals, semiconductors, ceramic conductors, and ceramic optical coatings in contiguous, large-area films and other specialized configurations. Fabrication strategies often rely on metallo-organic chemical vapor deposition (MOCVD) or related molecular-precursor approaches. Nanocrystalline semiconductor PV cells are generating much current excitement (3,4); their mesostructured charge-separation layers are deposited by molecular-precursor chemistry. Progress in deposition methods and conditions is important to improvement in substrate compatibility, prevention of interlayer diffusion, construction of nanometer-scale compositional profiles, and the accessibility of metastable phases – and therefore to PV-device performance. Large-scale production of new PV-cell designs will require processes that ensure environmental and health safety. All of these considerations depend critically on advances in molecular-precursor chemistry, and provide a strong rationale for DOE involvement.

This article surveys selected advances in molecular precursors to portray the main research directions in the field. Molecular-precursor chemistry is basic research that underpins all electronic-materials technologies, not just PV technology. Therefore, the view offered here is broad because the directions that will contribute most to specific DOE goals in the future cannot be confidently predicted. Recent developments are enabling deposition of electronic materials, such as high-T_c superconductors, that were either unknown or impossible to deposit just a few years ago, and are improving established semiconductor-growth processes. Recent developments are affording *selective* deposition, are allowing kinetic growth of previously unknown, metastable crystal structures, and are providing routes to high-quality semiconductor quantum dots (QDs), which are now being assembled into highly regular superlattice arrays. Recent developments are also supporting the growth of electronic materials at progressively lower temperatures, bringing fabrication of inorganic solids into the temperature regime of conventional organic chemistry. These developments, highlighted below, are ushering in the coming era of precise synthetic control over the crystal, nano-, and microstructures of electronic materials.

Discussion

MOCVD Precursors for Compound Semiconductors

The origins of molecular-precursor chemistry for electronic materials are found in the pioneering MOCVD studies of Manasevit and Simpson from the late 1960s (eqs 1 and 2) (5,6). The MOCVD of compound semiconductors has now become a mature research field, and has acquired numerous

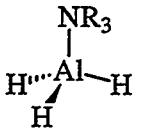
additional acronyms (OMCVD, OMVPE, MOMBE, CBE, etc.), some of which represent variations on the basic method (7-11). Precursors to III-V, II-VI, and related semiconductor materials may be divided into two categories: "conventional" precursors, which may simply replace one of the precursors used in the traditional dual-source approaches represented by eqs 1 and 2; and "single-source" precursors, in which both (or more) elements of a compound semiconductor are contained within the same precursor molecule. These categories are discussed below.

$$Me_3In + PH_3 \xrightarrow{\text{gas phase}} InP + 3CH_4 \quad (1)$$

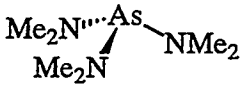
$$Me_3Ga + AsH_3 \xrightarrow{\text{gas phase}} GaAs + 3CH_4 \quad (2)$$

"Conventional" Precursors

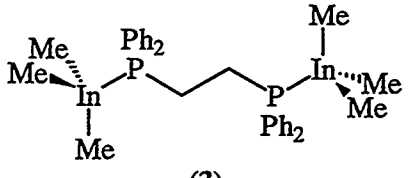
The primary goals of current research into conventional MOCVD precursors (7-11) for compound semiconductors are to reduce carbon incorporation, eliminate the use of toxic gases such as phosphine and arsine (PH_3 and AsH_3), and achieve higher precursor purities (8). Alternative alkyls like $GaEt_3$,and amine-alanes (**1**) or amine-gallanes (10,11) lead to lower carbon-impurity levels through more efficient elimination pathways or the absence of precursor metal-carbon bonds. The alkylated phosphorus and arsenic precursors *t*-$BuPH_2$ and *t*-$BuAsH_2$, and compound **2** may be used in place of phosphine and arsine (8); the tris(amino)arsine compound **2** affords lower carbon levels as well (8). Lewis base adducts like compound **3** are easier to purify and handle than are the parent metal alkyls, and liberate the purified metal alkyls upon mild heating for introduction into MOCVD reactors (10). Improvements of these kinds are leading to incremental advances in the growth of compound semiconductors.



(1)



(2)

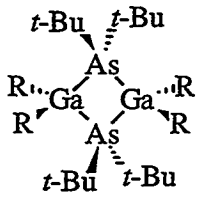


(3)

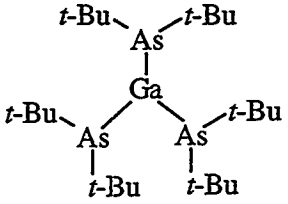
Single-Source Precursors

Proponents of the newer single-source-precursor approach suggest that it affords better stoichiometric control and lower growth temperatures than the traditional dual-source approach (12). Compounds **4** and **5** are representative examples of single-source precursors (for GaAs) taken from the work of Cowley, Eckerdt, Jones, and coworkers (12). Obviously, such precursors also eliminate phosphine and arsine from the procedures. The low volatilities of single-source precursors are their primary disadvantage, which preclude their use in standard atmospheric-pressure MOCVD. To date, the properties of semiconductor materials grown from single-source precursors have not equaled those of the best materials grown from traditional precursors; however, such comparisons are inherently unreasonable given the twenty years of optimization that have been invested in the dual-source approach. In view of this time investment, single-source precursors may have difficulty supplanting

the traditional precursors for compound semiconductors, but are likely to be more readily adopted for the growth of other families of electronic materials (see below).



(4)



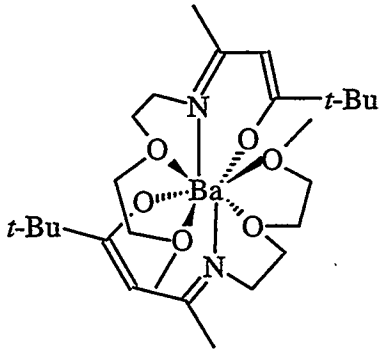
(5)

MOCVD Precursors for Oxide Ceramics

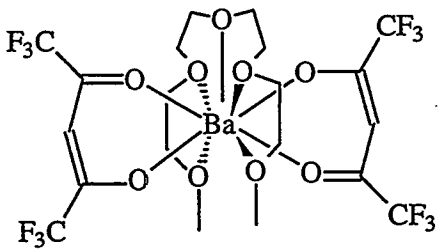
Following the successful MOCVD of semiconductors, considerable recent efforts have focused on extending the technique to electronic (oxide) ceramics, including superconductors, dielectrics, and electro-optics (13). This has proven to be considerably more challenging, largely because of a lack of suitably volatile, stable molecular precursors, but also because of the structural complexity of the oxide materials, which are typically ternary or quaternary phases. Even so, recent successes include the growth of $YBa_2Cu_3O_7$, $BaTiO_3$, Sr_2AlTaO_6, and $PbTiO_3$ as a few examples. The emergence of MOCVD of electronic ceramics represents an area of significant accomplishment in molecular-precursor chemistry.

Barium-containing oxide materials provide a good case study of the difficulties encountered in the growth of electronic ceramics. Barium is the prototypical example of metallic elements that are difficult to transport. In its conventional metallo-organic compounds barium behaves as a large dictation. It prefers the high coordination numbers of 8-11, but can bind only two mono-anionic ligands in its neutral compounds. Consequently, extensive ligand bridging produces the highly coordinated barium environments in conventional metallo-organics. Oligomeric, nonvolatile solid structures result, giving the metallo-organics poor precursor properties.

Molecular-precursor design is circumventing this coordinative-saturation problem through introduction of appropriate multidentate ligands (13-18). The compounds **6**, reported by Marks and coworkers (15), and **7**, reported separately by Meinema and coworkers (16), and Gardiner, Brown, and Kirlin (17), are two of several newly available precursors, which have been successfully used in the deposition of barium-containing electronic ceramics. They are not yet ideal precursors because of the partial thermal instability of **6** and the tendency of **7** to incorporate fluoride. Further advances in precursor design will extend the range and complexity of the electronic ceramics that may be grown by MOCVD.



(6)



(7)

Aerosol-Assisted and Spray CVD

What about electronic materials for which stable, volatile MOCVD precursors aren't available? New solution-delivery methods for MOCVD are appearing that make precursor stability and volatility less critical. Specifically, aerosol-assisted CVD (AACVD) (19) and spray CVD (20) function by generating a mist of a precursor solution. The mist is swept into a preheating zone where both solvent and precursor are vaporized just before entry into the reactor deposition zone. The difference in the two techniques is the method of mist generation: AACVD uses an aerosol droplet generator, whereas spray CVD uses ultrasonic nebulization. With solution-delivery methods, precursors are not directly volatilized from a compact solid phase but rather are first highly dispersed and volatilized in instants rather than after hours of heating.

Equations 3 and 4 provide example AACVD and spray-CVD procedures. The Ag(I) precursor in eq 3 (hfa = hexafluoroacetylacetonate; see compound **7**) lacks the *thermal stability* necessary for standard, direct-volatilization MOCVD. However, Ag films may be grown from eq 3 by AACVD as reported by Hampden-Smith, Kodas, and Xu (21). The Li-Nb double alkoxide $LiNb(OEt)_6$ lacks sufficient *volatility* for direct-volatilization MOCVD; yet, it deposits *epitaxial* $LiNbO_3$ from eq 4 by spray CVD as reported by Wernberg, Gysling, and Braunstein (20). AACVD and spray CVD facilitate use of single-source precursors, produce faster deposition rates than are obtained with standard MOCVD, and allow good stoichiometric control from mixed-precursor solutions (21). These methods are representative of advances in precursor delivery that are greatly expanding the range of compounds suitable for use as MOCVD precursors.

$$(hfa)AgSEt_2 \xrightarrow{\text{AACVD}} Ag + \text{byproducts} \quad (3)$$

$$LiNb(OEt)_6 \xrightarrow{\text{spray CVD}} LiNbO_3 + \text{byproducts} \quad (4)$$

Low-Temperature, Selective Metallization

Selective metallization refers to the deposition of metals on preselected substrate areas (growth surfaces) to the exclusion of others (nongrowth surfaces). Typically, growth surfaces and nongrowth surfaces differ chemically in ways that promote and prevent chemical deposition processes, respectively. Selective metallization is important in microelectronics research, and studies in the design of precursors able to provide growth selectivity are now emerging (22,23). These studies possess two common features that appear to be responsible for surface-selective deposition: (1) Clean, low-temperature processes for the MOCVD of metals, and (2) knowledge and control of precursor-surface interactions.

Clever chemical design is necessary in the development of MOCVD precursors that decompose cleanly at *low temperatures* to deposit metals. Identification of an efficient rearrangement and/or decomposition pathway is required. Two recent examples illustrate this point. Hampden-Smith, Kodas and coworkers have achieved selective Cu deposition at low temperatures by eq 5 (hfa = hexafluoroacetylacetonate; see compound **7**), in which Cu metal is generated by disproportionation (22). Gladfelter and coworkers have reported selective Al-metal deposition at low temperatures by eq 6; alane derivatives like dimethylethylamine alane are thermally unstable with respect to hydrogen elimination (23). Both eqs 5 and 6 proceed without impurity-generating ligand degradations, resulting in high-purity metals. In principle, low-temperature precursor-decomposition pathways could be designed for growing a wide range of materials such as ceramics and other covalent solids. However, when the growth temperatures fall significantly below recrystallization temperatures for

deposited materials, amorphous rather than crystalline deposits typically result, which are generally undesirable. Thus, low-temperature growth is particularly suited to deposition of metals having low recrystallization temperatures.

$$2LCu(hfa) \xrightarrow{120\text{-}200\ ^{o}C} Cu + Cu(hfa)_2 + L \quad (5)$$

$$L = PR_3, \text{ alkyne, etc.}$$

$$H_3Al(NMe_2Et) \xrightarrow{100\text{-}140\ ^{o}C} Al + 3/2H_2 + NMe_2Et \quad (6)$$

Growth selectivity is determined by the specific interactions of a precursor with the growth and nongrowth surfaces. Selectivity studies often employ metal growth surfaces and SiO_2 nongrowth surfaces as shown in Figure 1 (22,23). Hampden-Smith, Kodas and coworkers have found that LCu(hfa) precursors deposit Cu *nonselectively* on adjacent silica and metal surfaces (22). Surface characterization reveals that the precursor molecules form stable hydrogen bonds with surface hydroxyl groups on SiO_2 (Fig. 1a); this hydrogen bonding apparently leads to ligand dissociation and Cu nucleation on silica, which is intended to be the nongrowth surface (22). The LCu(hfa) precursors disproportionate rapidly on conducting metal surfaces (Fig. 1b), nucleating Cu there as well; hence, growth is nonselective. However, silylation of the surface hydroxyl groups on SiO_2 removes the hydrogen-bonding ability of that surface (Fig. 1c), precluding Cu nucleation and growth (22). Thus, the silica surfaces are easily passivated, providing good growth selectivity for the metallic surfaces. Gladfelter and coworkers have observed excellent selectivity for Al deposition on metallic growth surfaces in the presence of unpassivated SiO_2 nongrowth surfaces (23). Dimethylethylamine alane readily transfers H atoms to metallic surfaces (Fig. 1d), leading to H_2 elimination and Al nucleation. However, this precursor apparently reacts to form covalent interactions with hydroxylated silica surfaces (Fig. 1e), which prevent Al nucleation. In each of the cases represented by Fig. 1a — Fig. 1e, the specific precursor-surface interaction establishes whether or not surface metallization occurs.

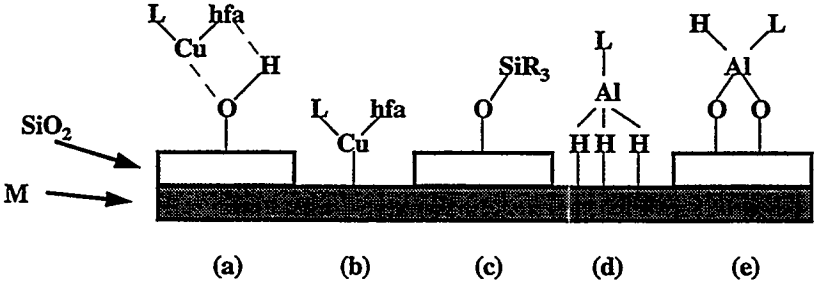


Figure 1. Precursor-surface interactions occurring on silica (nongrowth) and metallic (growth) surfaces (see text).

Low growth temperatures maximize the nucleation-rate differences on the growth and nongrowth surfaces resulting from the different chemical interactions, thereby enhancing growth selectivity. Additional fundamental studies into the development of low-temperature growth precursors and processes, and into the precise characterization of precursor-surface chemical interactions will be necessary for continued advances in selective deposition.

MOCVD of Metastable Phases

Solid-state syntheses of inorganic materials typically proceed under thermodynamic control; that is, the stoichiometries and crystal structures obtained are generally the most thermodynamically stable under the growth conditions (1,2). The various activation barriers separating precursors from the

thermodynamic and possible metastable crystal structures are generally all surmounted under the strenuous growth conditions required, such that all possible structures grow in thermodynamic equilibrium with one another. Thus, the thermodynamic structure is strongly favored in many growth methods.

Specific kinetic factors favor formation of metastable phases to a greater extent for thin-film growth than for other growth geometries. Lattice matching to a crystalline substrate may favor the nucleation and subsequent growth of a metastable crystal structure by MOCVD. Additionally, heteroepitaxial multilayer structures grown by MOCVD are only kinetically stabilized against layer interdiffusion to form more-complex, thermodynamically preferred, multinary phases. However, until recently no evidence indicated that structural features present in precursor molecules could influence the crystal structures of growing films. Barron and coworkers have recently obtained such evidence (24-26), which promises a previously unimagined level of synthetic control over metastable structures of electronic materials.

Barron and coworkers have grown a previously unknown cubic GaS phase from a gallium-sulfur cubane precursor, $[(t\text{-Bu})GaS]_4$, by MOCVD (eq 7) (24). The metastable cubic GaS converts to the thermodynamically stable hexagonal GaS phase upon heating to 550 °C. Related precursors having noncubic core geometries give either the thermodynamic hexagonal phase or an amorphous gallium sulfide (24). Only $[(t\text{-Bu})GaS]_4$, having a cubic Ga_4S_4 core, gives cubic GaS. Mechanistic studies under MOCVD conditions show that $[(t\text{-Bu})GaS]_4$ undergoes successive losses of *t*-Bu substituents, during which the robust Ga_4S_4 core remains intact (25). These observations support the proposed pathway in Fig. 2. Following elimination of *t*-Bu substituents, Ga_4S_4 units assemble into a cubic rock salt structure, which relaxes to a more-stable cubic zinc-blende structure (24). Thus the metastable crystal structure of the deposited GaS phase is determined by the core geometry of the molecular precursor.

$$[(t\text{-Bu})GaS]_4 \xrightarrow{390\ ^{\circ}C} \textit{cubic}\text{-GaS} + \text{byproducts} \quad (7)$$

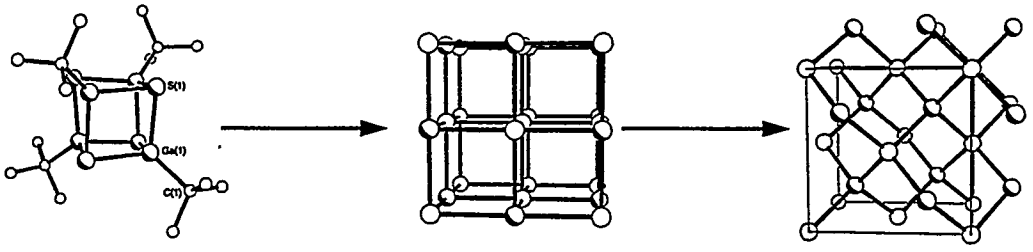


Figure 2. The transformation from cubane (Ga_4S_4) molecular precursor to cubic GaS material.

Barron's result has potentially far-reaching implications. Cubic GaS grown epitaxially on GaAs serves as the insulating gate layer in a gallium arsenide MISFET (26), demonstrating the technological significance of access to metastable electronic materials. We may expect that such access will become generally available. Barron and coworkers have prepared other metastable phases similarly, including tetragonal InS, cubic GaSe, and hexagonal InTe. Related indications of precursor-based kinetic control over the crystal structures of inorganic materials have begun to emerge from other laboratories as well, although such studies have yet to appear in the literature. I propose that kinetic control of phase growth will be best achieved by "soft" precursor-delivery methods such as AACVD and spray CVD (see above), which best preserve precursor structure during transport to the growth surface. Gaining control over structure is among the primary goals of

chemistry. Because this goal remains largely unmet in solid-state synthesis (1,2), "precursor-controlled MOCVD" is an exciting area that should be watched closely over the next several years.

Semiconductor Quantum-Dot Materials

Molecular-precursor routes currently provide the best syntheses of nanometer-sized semiconductor crystallites. These nanoclusters, nanocrystals, or quantum dots (QDs) exhibit strikingly different electronic and optical properties than do the corresponding bulk materials (27). Semiconductor QDs have size-dependent band gaps, electronic structures, and (discrete) optical spectra. Quantum confinement concentrates oscillator strength into narrow spectral regions, inducing significant nonlinear optical properties. These characteristics have allowed construction of novel QD LEDs (28,29) and consideration of QD-based optical switches. Additionally, QDs possess hydrogen-like excitonic wavefunctions, and so may be thought of as "artificial atoms" (27). Assembly of such artificial atoms into superlattice arrays having overlapping QD wavefunctions will lead to new, artificial electronic materials with engineered band structures (30). Such arrays may be useful for solar-energy conversion (3,4) and other applications. Remarkable achievements have been made recently in the synthesis of II-VI QDs, and related efforts in the synthesis of III-V QDs are progressing rapidly.

II-VI QDs

Bawendi and coworkers have prepared high-quality QDs of CdS, CdSe, and CdTe by controlled solution-phase nucleation and growth (eq 8) (31). The Bawendi procedure has been slightly modified by Alivisatos and coworkers (32). The important features of these syntheses are a La Mer growth mechanism (31) that provides monodispersity and size control, growth temperatures that are sufficiently high to induce excellent crystallinity, and lipophilic ligand capping of QDs (with TOPO/TOP) that affords surface passivation and solvent dispersibility. Although numerous prior II-VI QD syntheses exist, none produce materials of the quality obtained from the Bawendi procedure, which therefore sets the standard by which future QD syntheses must be evaluated. High quality QDs should conform to the following criteria: (*i*) they should be dispersible to confirm formation of discrete, unagglomerated particles; (*ii*) they should possess good crystallinity (by XRD) as deposited from solution/suspension; if annealing is required to induce crystallinity then criterion *i* should be re-established; (*iii*) they should be characterized by clear, single-particle TEM images; (*iv*) they should exhibit resolved spectral transitions to verify monodispersity. One may consider additional criteria, such as the observation of band-edge luminescence to demonstrate successful passivation of surface electronic states. This high level of quality will be necessary for most of the potential QD applications outlined above.

$$Me_2Cd + E(SiR_3)_2 \xrightarrow[TOPO/TOP]{200\text{-}300\ ^{\circ}C} CdE + 2MeSiR_3 \quad (8)$$

E = S, Se, or Te

II-VI QD Superlattices

The very narrow size distributions of the QDs prepared by eq 8 enable the growth of colloidal crystals, which are three-dimensional QD superlattices (30). Dispersions of CdSe QDs in octane/octanol become destabilized upon octane evaporation, resulting in "crystallization" of the QDs into face-centered-cubic superlattice arrays (eq 9). QD crystals with dimensions of up to 50 mm have

been obtained. Significantly, the interdot spacings in the superlattices depend on the sizes of the capping groups employed to stabilize the particles. Photoluminescence spectra confirm interdot overlap of QD electronic wavefunctions. Although a few prior examples of crystalline QD superlattices exist, the Bawendi work (30) is the first in which the QD size and superlattice spacing may be systematically varied. We may expect interesting properties of QD arrays to emerge from this very exciting development.

$$\text{CdSe QD dispersion} \xrightarrow[\text{-octane}]{\text{90\% octane, 10\% octanol}} \text{CdSe QD crystal} \quad (9)$$

III-V QDs

Micic, Curtis, Nozik, and coworkers have prepared high-quality QDs of InP and GaP (33). The syntheses are based on a set of chemical reactions (eq 10) developed primarily by Wells and coworkers over the past several years (34,35). When reactions of this type are conducted in TOPO/TOP (eq 11) under conditions that mimic the Bawendi synthesis (eq 8), QDs meeting the quality criteria described above are produced (33). Assembly of these III-V QDs into crystalline superlattices will likely be achieved in the near future.

$$MX_3 + E(SiMe_3)_3 \longrightarrow ME + 3Me_3SiX \quad (10)$$

M = Ga or In; X = halide; E = P or As

$$\text{"chlorometal oxalate"} + P(SiMe_3)_3 \xrightarrow[\text{TOPO/TOP}]{270\text{-}320\ ^oC} MP + 3\text{"}Me_3SiX\text{"} \quad (11)$$

M = Ga or In; X = Cl or oxalate

Low-Temperature Semiconductor Growth

Films or bulk crystals of II-VI, III-V, and group IV semiconductors are conventionally grown at the high temperatures of 550 – 1100 °C. Much current interest is directed to "turning down the heat" on the syntheses of covalent, nonmolecular solids, especially through design of molecular-precursor strategies (1). Such low-temperature processing may offer important advantages for the fabrication of electronic materials. Semiconductor film growth on thermally sensitive substrates such as optical polymers and plastics may become possible. Low-temperature processing will allow kinetic control over growth compositions, crystal structures, and crystal morphologies. The syntheses of size-controlled QDs described in the previous section provide good examples of the latter. Discovery of new, metastable crystal structures, potentially accessible at lower growth temperatures, will extend the range of available semiconductor band structures. Low-temperature processing will allow fabrication of thermally sensitive interfaces and heterolayer structures. Additionally, low-temperature processing should support growth selectivity as described above. In short, low-temperature processing will lead to new levels of crystal-structure and architectural control in the assembly of electronic materials.

The problem confronting low-temperature growth of semiconductor materials is the lack of suitable crystallization pathways for covalent, nonmolecular solids. Low-temperature crystal growth is normally conducted from saturated solutions; however, semiconductors have essentially no solubility

in conventional solvents. Consequently, semiconductors are typically grown at higher temperatures either from the gas phase (such as by MOCVD) or from the melt. Low-temperature processing requires development of new crystal-growth processes, two of which are described below.

Solution-Liquid-Solid (SLS) Growth

Buhro and coworkers have reported a new mechanism for the growth of crystalline InP, InAs, and GaAs whiskers and fibers at 203 °C and below, which are the lowest known growth temperatures for III-V materials (36). The synthetic medium, a suspension of low-melting, nanosized In or In/Ga droplets in an organic solvent, is the key to the crystal-growth pathway (Fig. 3). Catalyzed organometallic reactions are conducted in the organic-solvent phase depositing the elements of the III-V semiconductor into solution in the molten In or In/Ga flux droplets. The flux droplets become supersaturated, initiating III-V crystallization. Continued supersaturation-driven growth at the resulting liquid-solid interface produces the observed, quasi-one-dimensional crystal morphologies. This solution-liquid-solid (SLS) mechanism is named after the three phases involved (Fig. 3), and by analogy to the well-known vapor-liquid-solid (VLS) whisker-growth mechanism. SLS growth may become a useful means of generating a wide range of micro- and nanocrystalline semiconductors at low temperatures, perhaps including thermally sensitive, metastable compounds. If the technique can be modified to support thin-film growth, it may provide a chemical-bath-epitaxy approach to semiconductor fabrication.

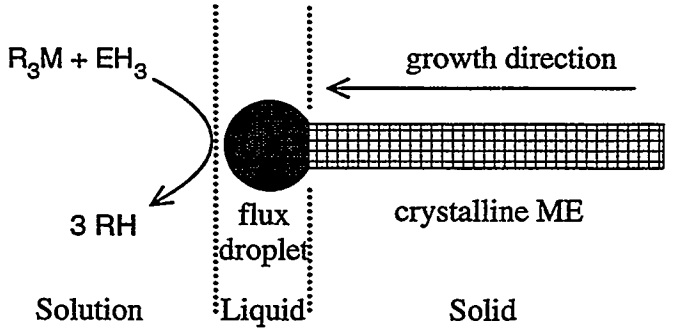


Figure 3. The solution-liquid-solid (SLS) growth mechanism; M = In, E = P or As; M = Ga, E = As; R = *t*-Bu.

Spray Deposition of QD Precursors

Schulz with a group at the NREL have reported a novel low-temperature semiconductor deposition strategy (37) that combines many of the themes and techniques discussed herein, and thus serves as an excellent final example. CdTe QDs are prepared by the method of Bawendi and coworkers (31). A solvent dispersion of the QDs is sprayed onto a heated substrate (Fig. 4) to produce densified polycrystalline CdTe films at nominal growth temperatures, ca. 200 °C lower than in conventional film-deposition methods (37). Two interesting considerations apply to this new growth method. First, QDs store excess energy in their surfaces, which is released exothermically upon sintering and grain growth. Hence, lower than usual substrate temperatures may be employed during deposition. Second, QDs may be thought of as molecular (cluster) precursors that contain significantly less organic ligation than do standard small-molecule precursors. Additionally, the ligands are datively bound as stable, closed-shell molecules in the QD precursors rather than as covalently bound radical fragments. Consequently, these surface-capping ligands should eliminate cleanly, potentially leading

to high-purity semiconductor films. Further studies should establish the degree of microstructural control that may be achieved in QD spray deposition, and if epitaxial film growth will be possible. The technique is at an early stage of development, and exciting progress may be anticipated.

Future Prospects

Continued efforts in molecular-precursor science will lead to important advances in the following areas. Electronic materials of increasingly complex structures and stoichiometries will be grown. Decreasing growth temperatures will afford kinetic routes to new metastable crystal structures. The production of a wide variety of ordered nanostructures will become possible, with QD superlattice arrays serving as the seminal examples. Significant control over the structures of surfaces and interfaces is likely to emerge, along with techniques for variously derivatizing crystal and crystallite surfaces to enhance optical and other properties. Increasing growth selectivities will allow assembly of complex materials architectures. Many of these developments will arise from new precursor-based growth techniques. In summary, rapid progress in materials chemistry is leading to new dimensions of structural control. The chemistry of the past century gave us control over the structures of molecules. The chemistry of the next century will give us control over the crystal structures, nanostructures, and microstructures of materials. These capabilities are essential to advances in PV-device technology and to other DOE goals of today and tomorrow.

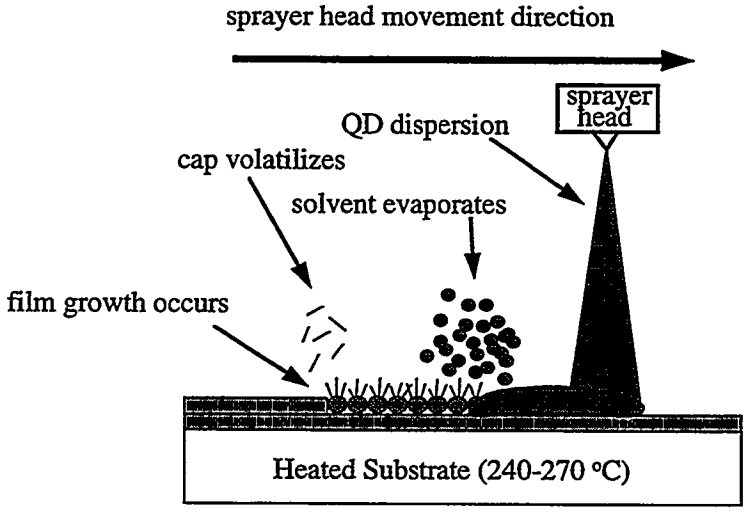


Figure 4. Low-temperature semiconductor film growth by QD spray deposition (37).

Acknowledgments

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PHOTOREDUCTION OF CO_2 USING METAL COMPLEXES

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Abstract

Photochemical reduction of CO_2 to fuels and chemicals is a challenging task. Work in the area of photochemical CO_2 reduction from the early 1980s to the present is summarized to provide a perspective on the achievements and problems involved in the process.

Introduction

Carbon dioxide fixation is an important area to study for the solution of problems related to the global environment and the depletion of fossil fuels. The chemical fixation involves conversion of recovered or separated CO_2 into useful chemicals and fuels. Economical fixation of CO_2 is only feasible if solar or hydraulic energy can be converted to chemical energy. There are several ways to use solar energy for CO_2 fixation: (1) solar-photochemical reduction of CO_2 typically to CO, $HCOO^-$, CH_3OH, and CH_4; (2) electroreduction of CO_2 [and water] using power generated by solar batteries typically to CO and $HCOO^-$ [and H_2]; (3) photoelectroreduction of CO_2 using semiconductors and surface-modified electrodes; (4) homogeneous and heterogeneous catalytic hydrogenation of CO_2 to methanol, formic acid, formamide, polymers, hydrocarbons, and others with solar generated H_2; and (5) genetically improved photosynthetic bacteria and algae-based CO_2 fixation [and H_2 production]. In this paper, we focus on photochemical reduction of CO_2 by homogeneous and microheterogeneous photocatalysts. Although many photo-induced stoichiometric reactions such as an insertion or addition of CO_2, reductive disproportionation to CO, metathesis of CN by CO_2, the formation of M-CO and M-OCHO complexes and in rare cases, the formation of M=O together with CO are known (1), we limit our discussion to photocatalytic reactions using metal complexes as catalysts. Photoinduced CO_2 fixation systems containing enzymes (2,3) are omitted.

Photocatalytic systems for CO_2 reduction

The potential for the reduction of CO_2 to $CO2^-$ is -1.9 V vs NHE, making the one-electron reduction mechanism highly unfavorable. In addition there is a large kinetic "overvoltage" for the one-electron reduction because of structural differences between linear CO_2 and bent $CO_2^{\cdot-}$. In contrast, proton assisted multi-electron steps are much more favorable:

$$CO_2 + 2H^+ + 2e^- \rightarrow HCO_2H \qquad E^\circ = -0.61\ V \qquad (1)$$

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O \qquad E^\circ = -0.53\ V \qquad (2)$$

$$CO_2 + 4H^+ + 4e^- \rightarrow C + 2H_2O \qquad E^\circ = -0.20\ V \qquad (3)$$

$$CO_2 + 4H^+ + 4e^- \rightarrow HCHO + H_2O \qquad E^\circ = -0.48\ V \qquad (4)$$

$$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O \qquad E^\circ = -0.38\ V \qquad (5)$$

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \qquad E^\circ = -0.24\ V \qquad (6)$$

Since the two-electron reduction to formic acid or CO requires a considerably lower potential than the one-electron reduction, electrolysis in the presence of catalysts can be carried out at considerably lower voltages. In the photochemical reduction of CO_2, the same considerations apply: the one-

electron reduction to $CO_2^{\cdot-}$ requires extremely strong reducing agents that are generally difficult to produce by photochemical methods.

Transition metal complexes have been used as photosensitizers and/or catalysts because: 1) they generally absorb visible light; 2) their excited states generally live long and promote rapid electron transfer; 3) their oxidation states accommodate multi-equivalent charge transfer to produce highly reduced and oxidized species; 4) they can provide vacant coordination site(s) for activation of small molecules. The systems used for photochemical CO_2 reduction can be categorized into several groups as shown below. The results from the various photocatalytic systems are summarized in Table 1.

Table 1. Photocatalytic Reduction of CO_2 [a]

Sensitzer	Catalyst or Relay	Donor	Product(s)	Φ	Ref.
$Ru(bpy)_3^{2+}$		TEOA	$HCOO^-$		4,5
$Ru(bpy)_3^{2+}$	MV^{2+}	TEOA	$HCOO^-$	0.01	6
$ReCl(bpy)(CO)_3$		TEOA	CO	0.14	7,8
$ReBr(bpy)(CO)_3$		TEOA	CO	0.15	10,11
$ReP(OEt)_3(bpy)(CO)_3$		TEOA	CO	0.38	13
$Ru(bpy)_3^{2+}$	Co^{2+}/bpy	TEA	CO, H_2		14
$Ru(bpy)_3^{2+}$	Co^{2+}/Me_2phen	TEA	CO, H_2	0.08	15
$Ru(bpy)_3^{2+}$	$Ru(bpy)_2(CO)_2^{2+}$	TEOA	$HCOO^-$	0.14	18-20
$Ru(bpy)_3^{2+}$	$Ru(bpy)_2(CO)_2^{2+}$	BNAH	$HCOO^-$	0.03 ($HCOO^-$)	18-20
			CO	0.15 (CO)	
$Ru(bpy)_3^{2+}$	$CoHMD^{2+}$	H_2A	CO, H_2		27
$Ru(bpy)_3^{2+}$	$Nicyclam^{2+}$	H_2A	CO, H_2	0.001 (CO)	28, 29
$Ru(bpy)_3^{2+}$	$NiPr\text{-}cyclam^{2+}$	H_2A	CO, H_2	~0.005 (CO)	31
$Ru(bpy)_3^{2+}$	bipyridinium$^+$, Ru colloid	TEOA	CH_4	10^{-4} (CH_4)	37, 39
$Ru(bpy)_3^{2+}$	bipyridinium$^+$, Ru or Os olloid	TEOA	CH_4	10^{-4} (CH_4)	37
			H_2	10^{-3} (H_2)	
p-Terphenyl	$Cocyclam^{3+}$	TEOA	CO, $HCOO^-$, H_2	0.25 ($CO+HCOO^-$)	47, 48
p-Terphenyl	$CoHMD^{2+}$	TEOA	CO, $HCOO^-$, H_2		34,48
Phenazine	$Cocyclam^{3+}$	TEOA	$HCOO^-$	0.07	52

[a] Abbreviations used: TEOA = triethanolamine, MV^{2+} = methylviologen, TEA - triethylamine, bpy = 2,2'-bipyridine, Me2phen = 2,9-Dimethyl-1,10-phenanthroline, BNAH = 1-benzyl-1,4-dihydronicotinamide, H_2A = ascorbic acid, cyclam = 1,4,8,11-tetraazacyclotetradecane and Pr-cyclam = 6-((N-R)pyridin-4-yl)methyl-1,4,8,11-tetraazacyclotetradecane where R = p-methoxybenzyl and benzyl.

(I) $Ru(bpy)_3^{2+}$ both as a photosensitizer and a catalyst

It was reported in 1985 (4,5) that visible light irradiation of $Ru(bpy)_3Cl_2$ (bpy = 2,2'-bipyridine) in dimethylformamide (DMF) - triethanolamine (TEOA) media containing CO_2 leads to efficient and preferential reduction of CO_2 to formate. The $Ru(bpy)_3^{2+}$ complex acts both as photosensitizer and as precursor of the catalytic species. Reductive quenching of the excited state of the $Ru(bpy)_3^{2+}$ by TEOA occurs, yielding the reduced Ru complex as shown in scheme I.

Scheme I. Reductive quenching

$$Ru(bpy)_3^{2+} + h\nu \rightarrow {}^*Ru(bpy)_3^{2+} \quad (7)$$

$${}^*Ru(bpy)_3^{2+} + TEOA \rightarrow Ru(bpy)_3^{+} + TEOA^{\cdot+} \quad (8)$$

$$TEOA^{\cdot+} + TEOA \rightarrow TEOA^{\cdot} + TEOAH^{+} \quad (9)$$

$$TEOA^{\cdot} + Ru(bpy)_3^{2+} \rightarrow TEOA_{ox} + Ru(bpy)_3^{+} \quad (10)$$

However the reduced Ru complex cannot reduce CO_2 directly in the one-electron transfer process which requires -1.9 V since the $Ru(bpy)_3^{2+/+}$ potential is -1.26 V. Since the presence of water enhanced the reaction with an optimum concentration around 0.015 M (~15 %), water may play a role in a photolabilization of bpy to form the active catalytic intermediate. The authors speculate that reduction of CO_2 to formic acid may involve the following sequential steps: 1) photogeneration of $Ru(bpy)_3^{+}$; 2) ligand photolabilization; 3) hydride formation by protonation: 4) insertion of CO_2; and 5) release of the formate produced. However, possible intermediates such as $Ru(bpy)_2(H_2O)(H)^{2+}$ and $Ru(bpy)_2(H_2O)(OCOH)^{2+}$ have not been characterized. Quantum yields were not reported.

An aqueous system containing $Ru(bpy)_3^{2+}$, methylviologen (MV^{2+}) and TEOA photoreduces CO_2 to formate with a quantum yield of 0.01 (6). In contrast to the previous system, the excited state of $Ru(bpy)_3^{2+}$ is oxidatively quenched by MV^{2+} to form $Ru(bpy)_3^{3+}$ and MV^{+} as shown in scheme II. However, direct electron transfer from MV^{+} to CO_2 is energetically impossible, since the reduction potential of $MV^{2+/+}$ is only -0.44 V. Although no mechanistic study was done, the authors suggest a mechanism which must involve proton participation as shown in eq. 1, since the pH of the CO_2 saturated solution is lower than pH 7. We believe the reactions 9 and 10 also produce $Ru(bpy)_3^{+}$ which can effect CO_2 reduction. The actual mechanism may be quite complicated.

Scheme II. Oxidative quenching

$$Ru(bpy)_3^{2+} + h\nu \rightarrow {}^*Ru(bpy)_3^{2+} \quad (7)$$

$${}^*Ru(bpy)_3^{2+} + MV^{2+} \rightarrow Ru(bpy)_3^{3+} + MV^{+} \quad (11)$$

$$Ru(bpy)_3^{3+} + TEOA \rightarrow Ru(bpy)_3^{2+} + TEOA^{\cdot+} \quad (12)$$

$$TEOA^{\cdot+} + TEOA \rightarrow TEOA^{\cdot} + TEOAH^{+} \quad (9)$$

$$TEOA^{\cdot} + Ru(bpy)_3^{3+} \rightarrow TEOA_{ox} + Ru(bpy)_3^{2+} \quad (13)$$

$$TEOA^{\cdot} + Ru(bpy)_3^{2+} \rightarrow TEOA_{ox} + Ru(bpy)_3^{+} \quad (10)$$

$ReX(CO)_3(bpy)$ or a Similar Complex as a Photosensitizer

$ReX(CO)_3(bpy)$ (X = Cl, Br) has been used successfully as a photocatayst for CO_2 reduction to CO with TEOA in DMF (7,8). When X = Cl, a quantum yield of 0.14 was measured in the presence of excess Cl^-. A formato-rhenium complex was isolated in the absence of excess Cl^-. It is known that $Re(bpy)(CO)_3H$ undergoes a slow thermal reaction with CO_2 to give the formato complex and the reaction is greatly enhanced by visible light (9). Detailed mechanistic studies (10,11) using $ReBr(CO)_3(bpy)$ with TEOA or TEA indicate that TEOA, TEA (triethylamine) and Br^- reductively quench the emission from the MLCT excited state of $ReBr(CO)_3(bpy)$ leading to prompt formation of $ReBr(CO)_3(bpy)^-$, which likely reacts with CO_2. $Re(CO)_2(bpy)\{P(OEt)_3\}_2^+$ is also a CO_2 reduction catalyst which produces CO with a quantum yield up to 0.38. Both the quantum yield and turnover number of the photocatalytic reaction are strongly dependent on the irradiation light intensity and wavelength (12). The photophysical behavior was studied by means of time-resolved UV-vis and IR spectroscopies (13). The photo-generated reduced catalyst, $Re(CO)_2(bpy)\{P(OEt)_3\}_2$, is also important for the activation of CO_2. However, in both $ReX(CO)_3(bpy)$ and $Re(CO)_2(bpy)\{P(OEt)_3\}_2^+$ systems it is still not known whether the CO_2 activation involves reactions such as: 1) formation of an unstable intermediate with vacant coordination site(s) from loss of CO, X^-, $P(OEt)_3$, or the bpy ligand from $ReX(CO)_3(bpy)^-$ or $Re(CO)_2(bpy)\{P(OEt)_3\}_2$; 2) formation of the CO_2 adduct from the unstable intermediate; 3) formation of the hydride species from the unstable intermediate followed by the insertion of CO_2.

$Ru(bpy)_3^{2+}$ as a Photosensitizer and Another Metal Complex as a Catalyst

It was reported in 1982 that a system containing $Ru(bpy)_3^{2+}/Co^{2+}$/tertiary amine as photosensitizer/catalyst/donor, respectively, is capable of catalytically generating CO (instead of formic acid) and H_2 by reduction of CO_2 and water under irradiation with visible light.[14] When TEA is used as donor, the system produces CO and H_2 in the ratio 0.68. The amount of gas (CO + H_2) produced and the CO/H_2 ratio depend markedly on the composition of the system and the amine used as donor. Addition of free bpy strongly decreases CO generation, but increases H_2 production. Higher selectivity for CO_2 reduction to CO was observed when TEOA was used instead of TEA.

The system was further studied by adding 4,4',6,6'-tetramethyl-2,2'-bipyridine or 2,9-dimethyl-1,10-phenanthroline instead of bpy (15). 2,9-Dimethyl-1,10-phenanthroline is particularly effective in promoting CO and H_2 formation, giving a quantum yield of 0.012 for CO and 0.065 for H_2.

Since the systems described above contain free bipyridine-type ligands, the formation of the Co(I) species from the excited state of $Ru(bpy)_3^{2+}$ in the $Ru(bpy)_3^{2+}/Co(bpy)_3^{2+}$/tertiary amine system has been examined in some detail (16). Stoichiomeric studies with $Co(bpy)_3^{+}$ and CO_2 were also carried out in order to elucidate the mechanism of the CO_2 reduction (16,17). It was shown that $Co(bpy)_3^{+}$ can be generated from $*Ru(bpy)_3^{2+}$ by various routes including reduction of $*Ru(bpy)_3^{2+}$ to $Ru(bpy)_3^{+}$ followed by reaction with $Co(bpy)_3^{2+}$, oxidation of the $*Ru(bpy)_3^{2+}$ by $Co(bpy)_3^{2+}$ to $Ru(bpy)_3^{3+}$ and, in principle, energy transfer to form $Ru(bpy)_3^{2+}$. The high-spin $Co(bpy)_3^{+}$ complex, which is substitution labile, is effective in reducing bpy to $bpyH_2$, H_2O to H_2 and CO_2 to CO (as the insoluble $[Co(bpy)(CO)_2]_2$), likely with $Co(bpy)_2(H_2O)H^{2+}$ and/or $Co(bpy)_2(H_2O)_2^{+}$ as intermediate. Unfortunately neither the CO_2 adduct nor the formato complex has been isolated.

Photochemical reduction of CO_2 has been achieved by using TEOA in DMF or the NADH model compound, 1-benzyl-1,4-dihydronicotinamide (BNAH) in H_2O/DMF, as a quencher in the presence of $Ru(bpy)_3^{2+}$ and $Ru(bpy)_2(CO)_2^{2+}$ (18,19). The system containing TEOA produces formate with a quantum yield of 0.14, whereas the system containing BNAH gave formate and CO with quantum yields of 0.03 and 0.15, respectively. The reduction potential of $Ru(bpy)_3^{2+}$ (-1.33 V vs SCE in DMF) is more negative than that of $Ru(bpy)_2(CO)_2^{2+}$ (-0.98 V) and nearly the same as $Ru(bpy)_2(CO)(COO^-)^+$ (-1.30 V). Therefore, $Ru(bpy)_3^{+}$ formed photochemically functions as the reductant of $Ru(bpy)_2(CO)_2^{2+}$.

$$Ru(bpy)_2(CO)_2^{2+} + 2e^- \rightarrow Ru(bpy)_2(CO) + CO \quad (14)$$

$$Ru(bpy)_2(CO) + CO_2 \rightarrow Ru(bpy)_2(CO)(COO^-)^+ \quad (15)$$

$$Ru(bpy)_2(CO)_2^{2+} + OH^- \rightarrow Ru(bpy)_2(CO)(COOH)^+ \quad (16)$$

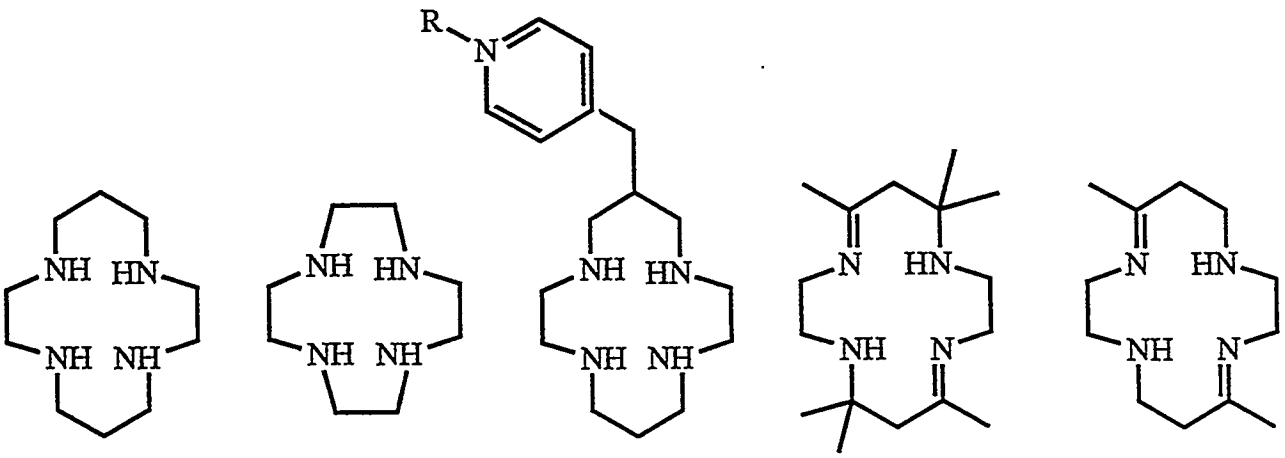
$$Ru(bpy)_2(CO)(COOH)^+ + OH^- \rightarrow Ru(bpy)_2(CO)(COO^-)^+ + H_2O \quad (17)$$

$$Ru(bpy)_2(CO)(COO^-)^+ + H^+ + 2e^- \rightarrow Ru(bpy)_2(CO) + HCOO^- \quad (18)$$

Suggested mechanisms (19) are shown in eqs. 14 and 15: the reduction of $Ru(bpy)_2(CO)_2^{2+}$ by two molecules of photogenerated $Ru(bpy)_3^{+}$ to yield CO with generation of $Ru(bpy)_2(CO)(COO^-)^+$ via $Ru(bpy)_2(CO)$ as shown in eqs. 14 and 15 in CO_2-saturated DMF. Based on their electrochemical studies (20), the authors propose (19) that the $HCOO^-$ is generated from $Ru(bpy)_2(CO)(COO^-)^+$ by a two-electron reduction involving participation of one proton as shown eq 18. They further explain (19) that the change in the main product from $HCOO^-$ to CO is due to acid-base equilibria among $Ru(bpy)_2(CO)_2^{2+}$, $Ru(bpy)_2(CO)(COOH)^+$, and $Ru(bpy)_2(CO)(COO^-)^+$ as shown in eqs. 16 and 17. It is widely believed that $HCOO^-$ forms by CO_2 insertion into the M-H bond in other cases. $Re(bpy)(CO)_3H$ reacts with CO_2 to afford $Re(bpy)(CO)_3OC(O)H$ quantitatively (21). $[Ru(bpy)_2(CO)H]^+$ reacts with CO_2 to form a formato complex, $[Ru(bpy)_2(CO)O(O)CH]$, which produces $HCOO^-$ upon another one-electron reduction.[22] The doubly reduced species $Ru(bpy)_2(CO)$ in eq. 14 may react with H^+ to form $[Ru(bpy)_2(CO)H]^+$, into which CO_2 may insert to form the

formato complex. However, it is reported that the catalytic systems composed of $Ru(bpy)_3^{2+}/Ru(bpy)_2(CO)_2$/BNAH and $Ru(bpy)_3^{2+}/[Ru(bpy)_2(CO)H]^+$/BNAH shows essentially the same reactivity (i.e., production rates and selectivity) in CO_2 reduction.[19] Both systems produce more CO than $HCOO^-$ ($CO/HCOO^- \approx 5$). As possible intermediates in the CO_2 reduction system, the molecular structures of $[Ru(bpy)_2(CO)_2](PF_6)_2$, $[Ru(bpy)_2(CO)(CO(O)OCH_3)](B(C_6H_5)_4 \cdot CH_3CN$ (as a model of $[Ru(bpy)_2(CO)(COOH)]^+$), $[Ru(bpy)_2(CO)(h\text{-}CO_2)]$, and $[Ru(bpy)_2(CO)(CH_2OH)]^+$ have been determined (23-26). However isolation of the formate complex formed by CO_2 insertion into $[Ru(bpy)_2(CO)H]^+$ has not been reported. It would be highly desirable to elucidate the detailed mechanism of formate and CO formation in this photocatalytic system (19) using time-resolved spectroscopies.

Photochemical CO_2 reduction to CO (and formate in some cases) has been reported (27-31) in a catalytic system using $Ru(bpy)_3^{2+}$ as the sensitizer, nickel or cobalt macrocycles (shown in Figure 1) as the electron relay catalyst, and ascorbate as a sacrificial reductive quencher. These systems also produce H_2 via reduction of water. When $CoHMD^{2+}$ is used as a catalyst at pH 4, the system produces a mixture of CO and H_2 with low selectivity (CO/H_2 = 0.06 - 0.3, depending on the conditions) (27). $Nicyclam^{2+}$ is reported to be an extremely efficient and selective catalyst for the electrochemical reduction of CO_2 to CO, even in H_2O (32,33). When $Nicyclam^{2+}$ is used as a catalyst in the photochemical system (28,29) however, the quantum yield of CO production is 5 x 10^{-4} at pH 5 and the selectivity, CO/H_2, is ~0.8. (The yield of both CO and H_2 are pH dependent and typically more H_2 is produced than CO.) $Nicyclam'^{2+}$ which is high-spin, six-coordinate with two cis water molecules, produces both CO and formate, while $Nicyclam^{2+}$, which is mainly low-spin, square-planar in H_2O, yields only CO from CO_2 reduction. $[Co^{III}L\text{-}H^-]^{2+}$ or $[Ni^{III}L\text{-}H^-]^{2+}$ (where L is a macrocyclic ligand) is suggested to be a common intermediate for CO and H_2 production in these photocatalytic systems, however, new studies (34-36) indicate that this may be incorrect (see section V).



cyclam cyclam' Pr-cyclam HMD DMD

Nicyclam complexes containing a pendant pyridinium group, which had been shown to function as effective mediators in the photochemical reduction of H_2O with a Pt colloid (37,38), were prepared and their catalytic behavior toward photochemical CO_2 reduction with $Ru(bpy)_3^{2+}$ was examined.[31] The system containing NiPr-cyclam^{2+} (R = p-methoxybenzyl and benzyl) at pH 5 evolved CO about 5 times more than that with underivatized Nicyclam^{2+}. The selectivity (CO/H_2= 0.1 - 0.65) depends on the conditions used, and typically more CO is produced with higher NiPr-cyclam^{2+} concentration.

$Ru(bpy)_3^{2+}$ and $Ru(bpy)_3^{2+}$-type complexes as photosensitizers in microheterogeneous systems

The photoreduction of CO_2 to methane and hydrocarbons is achieved in aqueous solution containing $Ru(bpy)_3^{2+}$, an electron donor, a bipyridinium charge relay, and Ru or Os colloids (37). The quantum yields for H_2 evolution (~10^{-3}) and hydrocarbon formation (~10^{-4} for CH_4, ~10^{-5} for C_2H_4 depend on the relay used. However, a similar system containing $Ru(bpz)_3^{2+}$ (bpz = bipyrazine) as sensitizer without a bipyridinium charge relay leads to the formation of methane, ethylene and ethane without the evolution of H_2 (37,39). The reduction of CO_2 is proposed to proceed via electron transfer followed by protonation of Ru- or Os metal-activated CO_2 rather than through a hydrogenation route, since no H_2 evolution occurs either in the presence of CO_2 or under argon with $Ru(bpz)_3^{2+}$.

Other metal complexes as photosensitizers

Photoreduction of CO_2 to formaldehyde and $HCOO^-$ has been carried out using an electron relay composed of trichlorobis(2,2':6',2"-terpyridyl)vanadium(III) as photosensitizer, MV^{2+} as electron acceptor, and ethylenediaminetetraacetic acid (EDTA) or TEOA as sacrificial electron donor (40). The quantum yields of photoproduction of formaldehyde are 0.036 and 0.051 with EDTA and TEOA, respectively, at 690 nm. The system is potentially photocatalytic, however the amount of formaldehyde and $HCOO^-$ produced are less than 10 % of the amount of photosensitizer used.

Since the one-electron reduction of CO_2 to $CO_2^{\cdot-}$ requires -1.9 V vs NHE, it is difficult to produce $CO_2^{\cdot-}$ by photochemical methods. The trinuclear cluster $[Ni_3(\mu_3\text{-}I)_2(dppm)_3]$ {dppm = bis(diphenylphosphino)methane} is reported to reduce CO_2 to $CO_2^{\cdot-}$ in THF when irradiated at $\lambda >$ 300 nm (41). Photolysis of $[Ni_3(\mu_3\text{-}I)_2(dppm)_3]$ in a 4:1 v/v THF/cyclohexene solution under 1 atm CO_2 led to oxidation of $[Ni_3(m_3\text{-}I)_2(dppm)_3]$ and to the formation of *cis*- and *trans*-1,2-cyclohexanedicarboxylates. Although the system is not photocatalytic, it is a rare case of purported involvement of $CO_2^{\cdot-}$. The authors assumed that the excited state of $[Ni_3(m_3\text{-}I)_2(dppm)_3]$ is quenched by CO_2 to form $CO_2^{\cdot-}$, however no photophysical study of $[Ni_3(m_3\text{-}I)_2(dppm)_3]$ is reported. Mechanistic and kinetic studies using time-resolved spectroscopies and measurements of the excited state potential are required to verify the claim.

Organic photosensitizers and ML^{2+} as catalysts

Irradiation of aromatic hydrocarbons such as phenanthrene, anthracene or pyrene in the presence of amine and carbon dioxide in aprotic solvents results in reductive carboxylation of the hydrocarbons

(42-44). The reactions are considered to proceed via the anion radical of the hydrocarbon reacting with CO_2 and then abstracting hydrogen to yield the corresponding product. Unlike these hydrocarbons, oligo(p-phenylene) ranging from *p*-terphenyl to *p*-sexiphenyl catalyze the photoreduction of CO_2 to $HCOO^-$ with TEA in a dried aprotic solvents such as DMF and CH_3CN (45,46). Although the apparent quantum yield is 0.072 with *p*-terphenyl, *p*-terphenyl concurrently undergoes photo-Birch reduction to form dihydroterphenyl derivatives and the system practically dies within 30 minutes. The turnover number for the formation of $HCOO^-$ is 4. However the addition of cobalt macrocyclic complexes suppresses the degradative photo-Birch reduction, and leads to efficient formation of both carbon monoxide and formate (47,48). When the $Cocyclam^{3+}$ complex is used, the total quantum yield for formation of carbon monoxide and formate is 0.25 at 313 nm in the presence of TEOA.

The kinetics and mechanism of CO formation in this system have been studied by continuous and flash photolysis techniques (34). Transient spectra provide clear evidence for the sequential formation of the *p*-terphenyl radical anion, the $Co^{I}HMD^+$ complex, the $[Co^{I}HMD\text{-}CO_2]^+$ complex and the $[S\text{-}Co^{III}HMD\text{-}(CO_2^{2-})]^+$ complex (S = solvent) in the catalytic system. These species together with the $[Co^{I}HMD\text{-}CO]^+$ complex, had previously been identified by various spectroscopic techniques including UV-vis, IR, NMR, XANES and EXAFS (35,36,49-51). The XANES study indicates that six-coordinate $[S\text{-}CoHMD\text{-}(CO_2^{2-})]^+$, in which a significant charge is transferred from metal to the bound CO_2, can be interpreted as a Co(III) carboxylate (51). The Co(I) complex transfers two electrons to the bound CO_2 moiety in this photocatalytic system (34). The electron-transfer rate constant for the reaction of *p*-terphenyl radical anion with the $Co^{II}HMD^{2+}$ is $1.1 ¥ 10^{10}$ M^{-1} s^{-1} and is probably diffusion controlled because of the large driving force (~ 1.1 V). Flash photolysis studies yield a rate constant of $1.7 ¥ 10^8$ M^{-1} s^{-1} and an equilibrium constant of $1.1 ¥ 10^4$ M^{-1} for the binding of CO_2 to $Co^{I}HMD^+$ in the catalytic system. These are consistent with those previously obtained by conventional methods in acetonitrile (35,49). The authors suggest that reactions 19-21 are responsible for the production of CO from $[S\text{-}Co^{III}HMD\text{-}(CO_2^{2-})]^+$ in the photolysis.

$$[S\text{-}Co^{III}HMD\text{-}(CO_2^{2-})]^+ + HA \rightleftharpoons [S\text{-}Co^{III}HMD\text{-}(COOH)^-]^{2+} + A^- \quad (19)$$
$$HA = TEA, MeOH, TEA^+$$

$$[S\text{-}Co^{III}HMD\text{-}(COOH)^-]^{2+} + \text{“}e^-\text{”} \rightarrow Co^{II}HMD^{2+} + CO + OH^- \quad (20)$$
$$\text{“}e^-\text{”} = Co^{I}HMD^+, Et_2NC^{\cdot}HCH_3,$$

$$OH^- + CO_2 \rightleftharpoons HCO_3^- \quad (21)$$

The slow step is likely to be the C–O bond breakage in the bound carboxylic acid with either $Et_2NC^{\cdot}HCH_3$, or $Co^{I}HMD^+$ acting as electron donor. Unfortunately the transient spectrum of $[S\text{-}Co^{III}HMD(CO_2^{2-})]^+$ is too weak topermit study of the proton dependence of its disappearance. Studies of catalytic systems with other cobalt macrocycles (34) highlight some of the factors controlling the kinetics of the photoreduction of CO_2. Steric hindrance and reduction potentials are important factors in the catalytic activity for photochemical CO_2 reduction.

Recently photoreduction of CO_2 to $HCOO^-$ (together with a small amount of CO and H_2) was achieved by UV-irradiation of the system involving phenazine (Phen) as a photosensitizer, $Cocyclam^{3+}$ as an electron mediator and TEA as an electron donor (52). The quantum yield for the formation of $HCOO^-$ is 0.07. Electron transfer from the photo-formed radical anion ($Phen^{\cdot-}$) to $Cocyclam^{3+}$ ($k = 4.3 \times 10^9\ M^{-1}\ s^{-1}$) results in the formation of $Cocyclam^{2+}$. Since the reduction potential of $Cocyclam^{2+/+}$ is ~-1.9 V vs SCE in CH_3CN, $Phen^{\cdot-}$ is hardly capable reducing Co(II) to Co(I). Therefore the authors suggest that: (1) $PhenH^{\cdot}$, produced by the protonation to $Phen^{\cdot-}$, may transfer a hydrogen atom to $Cocyclam^{2+}$ to form $Cocyclam(H)^{2+}$; and (2) the insertion of CO_2 into the hydride produces CO via the Co^{III}-formate complex. Although preliminary results appear to support the proposed mechanism, the hydrogen atom transfer step needs to be investigated in detail.

Comparison between thermal hydrogenation and photochemical reduction of CO_2

In the early 1970's, several groups found that formic acid, esters, and amides can be prepared from carbon dioxide, hydrogen, and a third component (in many cases) in the presence of homogeneous transition metal (Ti, Ru, Rh, Pd, etc.) catalysts including Wilkinson's catalyst $[Rh(PPh_3)_3Cl]$ (53,54). These reactions were carried out under a range of total gas pressure of 20 - 200 atm in the temperature range of 24 to 160°C. For example, when $[RhH(COD)]_4$ (COD = cycloocatadiene) is used as the catalyst precursor with TEA and dppb (dppb = $Ph_2P(CH_2)_4PPh_2$) as additives in DMSO under a total ($H_2 + CO_2$) pressure of 40 atm at room temperature, the system produces $HCOO^-$ with the turnover number of 2200 in 18 hrs. The TOF (turnover frequency), which is defined as the maximum initial rate of reaction per mole of catalyst, reaches 390 h^{-1} (55). Various solvents were used for homogeneous hydrogenation of CO_2 to formate including supercritical CO_2. In supercritical CO_2 with $RuH_2[P(CH_3)_3]_4$, TEA , and water, the remarkable TOF of 1400 h^{-1} was obtained (56). Mechanisms of formate (or formic acid) formation via CO, or carbonate, or hydride transfer to CO_2 were considered in some cases. However, the mechanism involving CO_2 insertion into a M-H bond is widely proposed. The reactive intermediate with vacant coordination site(s), derived from the metal catalyst, reacts with hydrogen to generate the metal hydride, followed by CO_2 insertion to form the formato complex. More detailed mechanistic and kinetic studies are needed.

Photochemical CO_2 reduction is normally carried out under 1 atm CO_2 at room temperature. Therefore the concentration of dissolved CO_2 in the solution is quite low (e.g. 0.28 M in CH_3CN and 0.03 M in water). Under photochemical conditions, TON (which is defined as the maximum number of moles of product per mole of catalyst) and TOF are dependent on irradiation wavelength, light intensity, irradiation time, and catalyst concentration. In fact, the TON and TOF are sometimes derived from different experiments. They are not optimized in most photochemical experiments. Since the concentration of the actual catalyst is not known in some cases, it only gives some guidance in estimating the catalytic activity. The typical range of the apparent TOF for CO or $HCOO^-$ formation can be calculated to be 0.1 to 10 h^{-1}, except for the $Ru(bpy)_3^{2+}/Ru(bpy)_2(CO)_2^{2+}$ system, in which the apparent TOF reaches 180 h^{-1} based on $[Ru(bpy)_2(CO)_2^{2+}]$. Typically the photochemical reactions are monitored up to one day. Both apparent TOF and TON in photochemical CO_2 reduction systems seem smaller than those in hydrogenation reactions. The rates of the catalytic reaction and the catalyst stability are important issues for photochemical CO_2

reduction. The rate-determining step or steps for photochemical CO_2 reduction are not known. It is believed that dark reactions including bond formation and bond cleavage are much slower than photoexcitation or subsequent electron transfer reaction.

Can the catalysts in the photochemical system be replaced by catalysts used for hydrogenation in order to speed up the dark reaction? In photochemical methods, an oxidative addition of a proton to the reduced metal center (that typically forms by photo-induced electron-transfer) gives a metal hydride species, however, in hydrogenation methods the metal center with vacant coordination site(s) seems to react with H_2. Some dihydrogen adducts of the metal complexes have been shown to be in equilibrium with the hydride species. It would be desirable to study the properties and reactivities of such complexes in order to find better catalysts for CO_2 reduction and hydrogen production..

The area of hydrogenation of CO_2 to HCOOH, esters, amides, alcohols, and hydrocarbons with homogeneous and heterogeneous metal catalysts is currently under active study and is promising to some degree. However, can we find a cheap and clean source of H_2? At present, hydrogen is manufactured by thermal cracking of oil resources, consuming fossil fuels as well as generating carbon dioxide. Therefore we need to develop technologies to produce H_2 using solar energy.

Challenge for photochemical CO_2 reduction and water splitting

Solar energy conversion is a formidable problem. The system must satisfy the following conditions: (1) strong absorption in the visible region; (2) long-lived excited state; (3) efficient quenching of the excited state to produce highly reduced and oxidized intermediates; (4) no harmful side reaction to deactivate the photosensitizer or catalyst/mediator; (5) ability to undergo multi-electron transfer; (6) long-lived intermediates [or catalyst] to promote bond formation and cleavage reactions to desired products [These dark reactions are much slower than photo-process.]; and (7) combining oxidizing and reducing cycles [to avoid the use of a sacrificial reagent]. Although conditions 1 to 6 have been fulfilled to some degree, to our knowledge all previous attempts with homogeneous catalysts have failed to achieve condition 7 (except one report (57) about water splitting). Do we need to design organized systems modeled upon natural photosynthesis? Should we accept a small TOF as nature does? What kind of catalyst can accommodate the four-equivalent charge for O_2 or HCHO production? How can we effectively couple the reduction or oxidation reactions with proton-, hydrogen-atom- or hydride-transfer reactions to lower the reaction barrier? Many questions still need to be answered in order to achieve efficient photochemical CO_2 reduction and water splitting.

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REVISITING THE SOLAR HYDROGEN ALTERNATIVE

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Abstract

Research aimed at the development of technology to advance the solar-hydrogen alternative is per definition mission oriented. The priority that society puts on such research rise and fall with the priorities that we associate with the mission. The mission that we associate with the hydrogen economy is to provide a technological option for an indefinitely sustainable energy and material economies in which society is in equilibrium with its environment. In this paper we try to examine some global aspects of the hydrogen alternative and recommend formulation of a "rational" tax and regulatory system that is based on efforts needed to restore the ecological balance. Such a system, once entered into the price structure of the alternative energy schemes, will be used as a standard to compare energy systems that in turn will serve as a base for prioritization of publicly supported research and development

Introduction

Among the various sections in this workshop, two are dedicated to single small molecules - CO_2 and H_2. The focus of the CO_2 program is to mimic the natural photosynthetic process by creating technology to utilize CO_2 as a chemical feedstock for synthesis of carbon- based chemicals. The essence of the hydrogen program is to create an energy technology that will eliminate the need to have CO_2 as the end-product of the energy utilization cycle.

Figure 1 describes schematically an idealized global energy cycle that will allow the planet to reach sustainable equilibrium. The energy cycle will be limited by thermodynamics, with the solar energy as a sole supply, while the material cycle required to support the energy cycle will constitute a closed system that does not leave any residue.

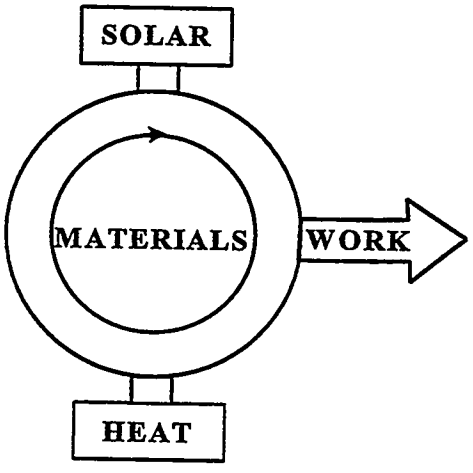


Figure 1 Schematic Representation of Idealized Ecology of Energy Use

Three alternative cycles that might satisfy such requirements are shown schematically in figure 2:

The first cycle is the Hydrogen cycle, details of which will follow. On the material side it involves the reversible use of water, hydrogen and oxygen. Solar energy is used, directly or indirectly, as the energy source needed to photolyze water to hydrogen and oxygen. Combustion of the hydrogen back to water produces the required energy. Two combustion mechanisms are shown, high temperature combustion and low temperature combustion through fuel cells. Although the balance of water - hydrogen - oxygen is cyclical, the high temperature combustion will produce oxidized nitrogen that will leave unwanted residues.

The second cycle is completely based on electrical power with no consumable materials. Again, the full cyclicity is illusionary - it is based on ideal reversibility and an infinite lifetime of the secondary batteries.

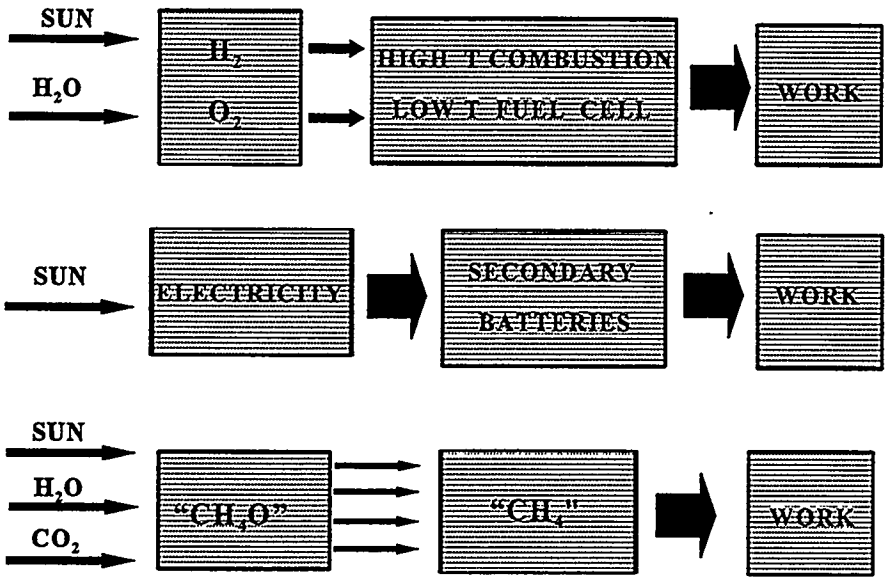


Figure 2 Alternative Cyclical Energy Pathways.

The third cycle is the carbon cycle, in which the high energy intermediates can be various reduced carbon compounds such as hydrocarbons and alcohols while the low energy end product is CO_2. Creating an effective technology to reduce CO_2 back to the high energy intermediates can close this cycle.

Why Hydrogen?

Among the various possible energy cycles, the water-hydrogen cycle has attracted special attention.

Presently, most of our energy needs are satisfied through the carbon route using non- renewable energy sources and leaving the low-energy end product in the atmosphere. The possibility of replacing the carbon-based energy technology with a hydrogen based technology has attracted the imagination of scientists and the general public since the non-sustainability of the present energy system became apparent. Some of the reasons for the popularity of the concept are shown in figure 3.

The apparent cyclicity and simplicity were previously discussed. In addition, the Hydrogen Economy offers the potential of a smooth transition from fossil fuels, especially natural gas, making use of a significant fraction of the available infrastructure. It is easily scalable. It depends heavily on the

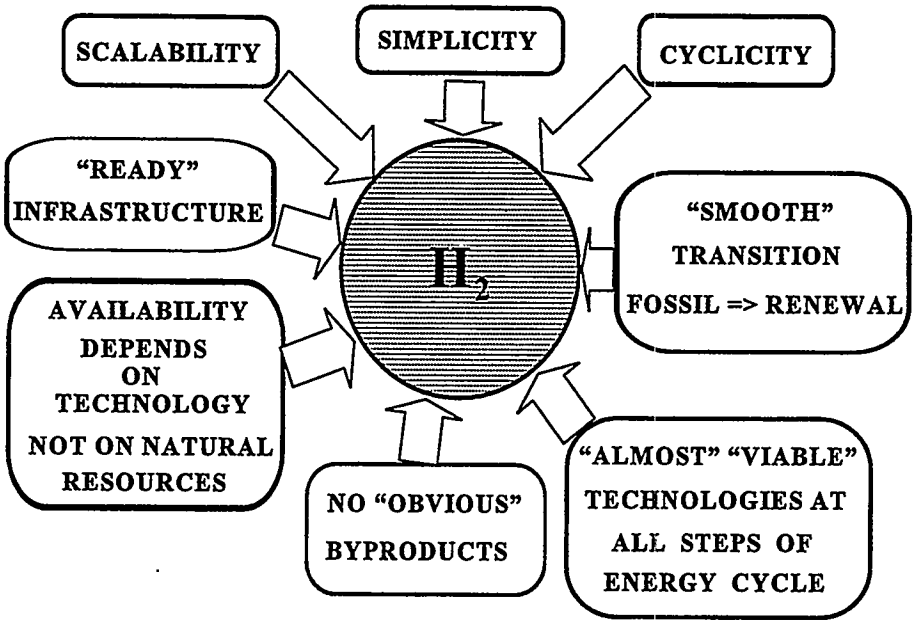


Figure 3 Convergence of Attractions of Hydrogen Based Economy

availability of cost-effective technology and not on availability of natural resources, an aspect very attractive to the developed countries.

In addition to all the legitimate reasons that hydrogen is considered a viable alternative to fossil fuels as the ultimate energy carrier, there is the unescapable sense that much of the attraction of the Hydrogen-Water cycle is similar to the unending attraction of perpetual motion machines throughout history. A random cruise through the Internet shows that significant portion of the discussions center around the concept that since one can obtain hydrogen by "simply" "stripping" it from water - the only impediment from universal use are special interest groups that benefit from fossil- fuel based economy.

Hydrogen Based Economy:

An attractive feature of the hydrogen based economy is that one can identify viable technologies at every stage of the energy cycle with the main impediment for implementation being the cost-effectiveness in comparison with existing alternatives. The elements of such a hydrogen-dependent energy cycle are shown in figure 4.

The uniqueness of Hydrogen rests both at the output of the energy cycle, when the energy is released by oxidation back to water, and the input part in which water is used as the material source. The essence of the solar-hydrogen alternative is that the ultimate source of the energy is solar while hydrogen is used to relay this energy to the consumer. In between these two steps many alternatives exist. In the US, and many other countries, tests are being conducted to investigate the characteristics of the entire system [1] with attempts to identify segments that can be economically reduced to practice at the earliest opportunity.

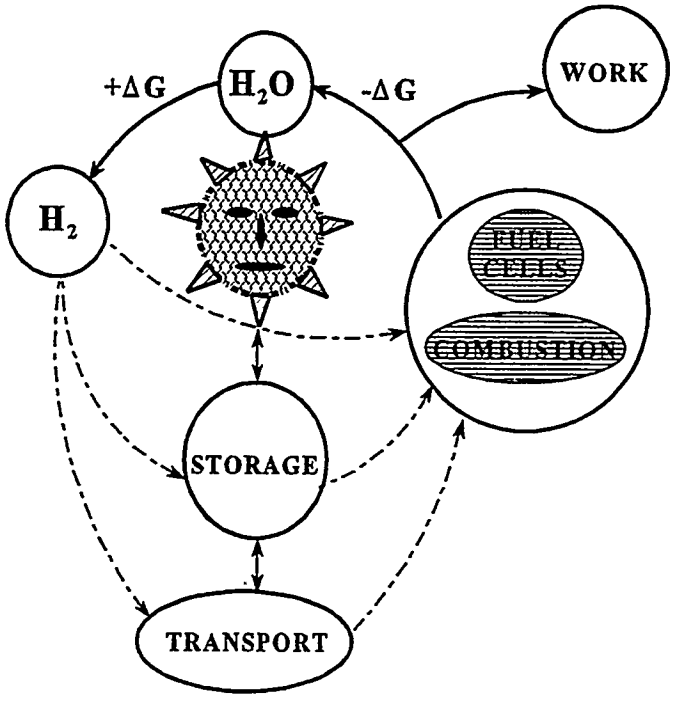


Figure 4 Schematic Representation of the Elements of Hydrogen Based Economy.

Solar Hydrogen Production:

There are various way to classify solar hydrogen production. Our panel (B2) chose the following categories (see the panel report):

- Photovoltaic or Photoelectrochemical Solar Cells Coupled to Water Electrolyzers
- Photoelectrolytic Systems
- Photochemical Homogeneous and Microheterogeneous Systems
- Photobiological Systems

Some details about the specifics of the various approaches can be found in the panel report. Here we would like to consider some global aspects that might have implications on the research priorities in these areas.

From the perspective of a cyclical hydrogen economy that draws its energy from the sun, it doesn't really matter whether the production is direct, namely through some photochemical means in which the water is photolyzed to hydrogen and oxygen, or indirect approach in which the light will be absorbed by a solid state device to produce photovoltage (photovoltaic cell) or high temperature (photothermal device). Schematic representation of the two routes is shown in figure 5. From an ecological perspective, there is no identifiable difference between these approaches, so the issue reduces to cost, efficiency, scalability, etc. The homogeneous route of direct photolysis of water to hydrogen and oxygen is frequently described as the Holy Grail of photochemistry. It is represented in figure 5A by the dual role of water as a donor and an acceptor. The scientific literature is cluttered

with nonreproducible success reports. The recent reported success by Katakis et.al. [2] is causing a great deal of interest but as of now (four years after publication) there are no reported attempts to reproduce this work. More typical and reproducible are examples that use sacrificial donors. In many of these cases the absorber is a ruthenium-based dye, the catalyst is platinum and a typical relay is a dye such as Methyl-Viologen [3]. To contrast these heroic efforts, the option represented in figure 5B can be exercised easily by high-school students by purchasing a commercial solar cell and connecting it to two platinum electrodes. The best demonstration of some of these issues can be traced to the comparison of photovoltaic cells connected to an electrolyzer and photoelectrochemical devices made of photovoltaic cells in which the catalyst is directly deposited on the cell and the device is immersed in the electrolyte. More detailed discussion of these devices is presented in the panel report. Occasionally this issue is referred to as the "wire issue". From the first days of photoelectrochemistry, after it was demonstrated by Fujishima and Honda [4] that TiO_2 can directly photoelectrolyze water, the question was raised [5] whether there are intrinsic advantages over the indirect approach of connecting photovoltaic cells to an electrolyzer. Junction formation is easier with photoelectrochemical devices while stability is much less of a problem with the indirect approach. An interesting, and not surprising, aspect of this debate is that advocates for the various approaches can be easily identified with their respective academic disciplines. "Pure" chemists want to stay with their solutions and many physicists and engineers don't want to hear about anything wet. Controlled experiments in which the same systems are being tested with and without "wires" are hard to find.

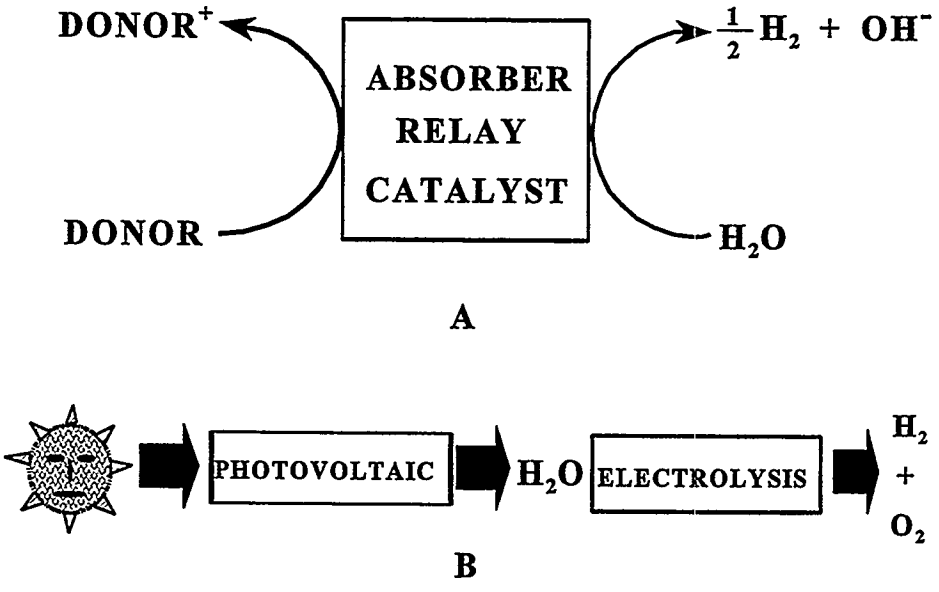


Figure 5 Schematic representation of photolysis of water through A. Direct photolysis of homogeneous and. microheterogeneous solution. B. Indirect photoelectrolysis with a photovoltaic cell and an electrolyzer.

Summary and Recommendations

Research aimed at the development of technology to advance the solar-hydrogen alternative is per definition mission oriented. The priority that society puts on such research rises and falls with the priorities that we associate with the mission. In this kind of research; science, technology, and economic analysis, cannot be easily separated. It is easy to purchase a simple photovoltaic cell, connect it to two platinum electrodes and produce hydrogen with a reasonable efficiency. The problem is that this hydrogen, and its associated stored energy, will be very expensive. Most of the various schemes that we have discussed to photolyze water are being pursued with the hope of significant improvement in the economics.

Conventional Analysis (see for example the Bolton report [6]) starts from an assumption that because of the diffuse nature of the solar radiation and the collection requirements, the minimum practical conversion efficiencies of any solar-hydrogen conversion scheme should be 10%. This analysis is based on present price of hydrogen derived from fossil fuels and present energy prices. The argument follows that any technology that is not within striking distance of such efficiency should not receive priority in funding. Based on this assumption - it was recommended that solid-state schemes such as photovoltaic-electrolyzer and photoelectrochemistry have the best potential, followed by bioconversion and value-added schemes in which the economy is determined by a different requirement, such as water purification, and the hydrogen is just valuable a by-product

The analysis does not take into account the fundamental mission of solar-hydrogen development which is to provide a technological option for an indefinitely sustainable energy and material economies in which society is in equilibrium with its environment. This mission is part of the vision of everyone involved in this research and is the main reason for maintaining a separate research program in this area. But the non-cyclicity of alternative energy schemes and the residues that we leave do not enter the beneficial analysis of the various schemes mainly because we are unable to price them.

Environmental laws and environmental economics are being pursued largely independently from the scientific and technological efforts. The net result is a language gap in which information is not being shared. It is urgent that a multidisciplinary effort will initiate communication to formulate a tax and regulatory structure that will scale with the impact on the environment and the total cost to society that will be required for restoration. This "rational" tax and regulatory system will be used as a standard to compare energy systems and will serve as a basis for prioritization of publicly supported research and development. The reduction to practice of this kind of tax system will depend on the political climate, but such is also the case for the technology. In both cases our role is to provide viable options for the political and economic establishments that will provide them with the tools to balance these options against other needs.

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HETEROGENEOUS PHOTOCATALYSIS FOR AIR AND WATER TREATMENT: FUNDAMENTAL NEEDS FOR QUANTUM EFFICIENCY ENHANCEMENT*

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PRESENTED AT DOE WORKSHOP: "Research Opportunities in Photochemical Sciences," Estes Park, Colorado, Feb. 5-8, 1996. Heterogeneous Photocatalysis for Air and Water Treatment: Fundamental Needs for Quantum Efficiency Enhancement.

Introduction

In the remediation industries, a useful treatment technology must be "general, robust, and cheap"(1). Among oxidation processes, heterogeneous photocatalysis is now broadly demonstrated to destroy common water and air contaminants (2). The potential process uses of highly stable titania, long lived lamps (one year), and room temperature operation, indicating a simple and robust process. We are left to address the third criterion: Can photocatalysis be "cheap"?

In both liquid phase and gas phase treatment and purification by photocatalysis, it is established that the primary barrier to commercialization is often cost. Cost in return is dominated by the efficiency with which solar or lamp photons are harvested for productive light, and subsequent dark, reactions. This paper therefore defines fundamental needs in photocatalysis for pollution control in terms of activities which could lead to quantum efficiency enhancement.

We first recall three related definitions. The quantum yield (QY) is the ratio of molecules of reactant converted per photon absorbed (3), a fundamental quantity. A less fundamental, but more easily measured variable is the quantum efficiency (QE), the ratio of molecules converted per photon entering the reactor (3). A third variable is the energy required per order of magnitude pollutant reduction, or EEO (4), a definition which provides for easy energy cost comparisons among different technologies. Each measure cited here reflects the photon, and thus the electrical, cost of this photochemistry.

We consider here several approaches to increasing the quantum efficiency, QE, of a heterogeneous photocatalysis. These are:

- PROCESS INTEGRATION: Use photocatalysis (or other chemical oxidation process) to carry out attack of a recalcitrant pollutant, then use a cheaper, biological process to mineralize the resultant more biodegradable intermediates (5).

- FEED CONDITIONING: Use additives which enhance quantum efficiencies, either through provision of more active oxidants (e.g., ozone (6) vs. oxygen) or through use of a more productive pathway, e.g., a photo-initiated chain reaction (7) rather than a photo-stoichiometric, non-chain oxidation.

- PERIODIC OPERATION: Use alternating light/dark operation to improve the selectivity with which photo-produced active intermediates, e.g., electrons (e-) and holes (h+), are utilized productively (8).

- REACTION INTEGRATION: follow the industrial photochemistry adage of matching the chemistry to the photon source. This notion is exemplified by the recent Solarchem homogeneous oxidation process (9), which combines a broadly photoexcitable iron-oxalate actinometer with a dark iron-peroxide Fenton chemistry to achieve an efficient, solar-driven generator of oxidation power. Similarly, the use in gas-solid photocatalysis of semiconductors such as tungsten trioxide, with a broader solar action spectrum that titania, could considerably enhance utilization of solar and lamp photon resources.

Quantum Efficiency Enhancement via PROCESS INTEGRATION

Single treatment techniques rarely accomplish the entire remediation task, and a sequence of operations is required. For example, an early process proposed for removal of 40ppb of PCBs in water (10) envisioned contains multiple technologies: (a) a flow equalization tank to accommodate variable volumetric feed rates, (b) filters to remove fine particles, and © activated carbon for removal of trace dissolved organics, including PCBs. Other unit operations included (d) a decantation tank to allow phase separation of aqueous from non-aqueous phases, (e) an incinerator for combustion of loaded carbon and waste sludge, and (f) a heat recovery and gas scrubber unit to complete the incineration train.

Photochemical destruction technologies may logically be targeted to replace the activated carbon bed, especially where the latter performs poorly, as for adsorption of low molecular weight halogenates (TCE, PCE, etc.) which bind weakly to carbons. In the PCB case illustrated, a prior process economics comparison of carbon vs UV-ozone (10) was augmented to include photocatalysis (11). With the proviso that the apparent quantum efficiencies of photocatalysis vs UV/ozone were the same, the latter substitution was predicted to provide a lower cost process, albeit only comparable to carbon, even when long lived lamps and only minimal labor for inspection and lamp changes were assumed. This example emphasizes the need for highly efficient, and long lived lamps, and for a high quantum efficiency process for effective water treatment.

A combination of oxidation technologies may be more efficient than a single approach. For example, more than fifty studies have found that a chemical pre-oxidation enhances a subsequent biotreatment, usually bio-oxidation (5). These studies were primarily suggestive, often involving

only one chemical and one biological conversion (e.g., oxidation), over a narrow range of variable(s) (treatment time, oxidant concentration, etc).

If we identify only photolysis, ozonation, peroxidation, UV-ozone, UV-peroxide, photocatalysis, and ozone-peroxide as chemical treatments, and consider biological alternatives to be activated sludge, pure culture oxidation, anaerobic digestion, trickling filter, and soil column operations, these seven chemical oxidation and five common biotreatment possess 35 independent two step chemical plus biological oxidation possibilities. The fundamental research surface is hardly scratched here: which photochemistries most efficiently generate the most biodegradable, and least toxic, early intermediates?

Recent modeling efforts (12a,b,c) have begun to indicate operating regions where a smaller total volume or total cost is achieved with two steps process((photo)chemical plus bio-oxidation) instead of one (photo)chemical oxidation step. More photochemical work is needed here to establish the full range of intermediates, as well as their biodegradability and biotoxicity (if any), expected from characteristic recalcitrant pollutant structures, so that concurrent biodegradation efforts can be executed in both laboratory and modeling.

We expect industry to use a technology only where it is clearly advantageous. A photocatalytic insert may improve ongoing processes for water or air treatment. For example, many manufacturing sites use on-site biological ponds, lagoons, or related low technology water treatment.

The integration of a smaller (photo)chemical unit upstream to render one recalcitrant and/or appreciably biotoxic feeds more biodegradable could enhance the individual efficiencies of both the photoreactor and the biotreatment plant.

Quantum Enhancement Opportunities: AIR

In the gas phase remediation of air, photocatalysis remains the only current emerging phototechnology option. (If e-beams are allowed as "photo"chemistry, then the e-beam treatment used commercially to remove pollutants from power plant exhausts deserves inclusion as well.) For photocatalysis, the Miller/Fox economic estimates (13) of 1993 demonstrate that high quantum efficiencies are again the central process requirement; the photocatalytic treatment of candidate air streams which contain low levels of high quantum efficiency contaminants (e.g., trichloroethylene, perchloroethylene, ethanol and methanol) was predicted to compete favorably with activated carbon, and with catalytic and thermal incineration (13). Lower quantum efficiency examples provided unfavorable economics. More recent estimates from NREL have confirmed this conclusion for air remediation processes (14).

Enhancement via FEED CONDITIONING

Two approaches have been reported. The first is addition of ozone, a more reactive oxidant that molecular oxygen, to the contaminated air feed to a photocatalytic reactor. The second involves

addition of chlorinated olefins to previously contaminated air; this latter approach is general against a broad range of contaminant structures (aromatics, alcohols, aldehydes) but is not universal; each new compound requires testing.

It is counterintuitive to add a new contaminant (e.g., ozone or perchloroethylene) to an already contaminated stream in order to enhance a desired rate, especially if the added specie is itself hazardous. History provides an important and commercial counterexample to this logic: the addition of gaseous ammonia to combustion exhaust streams containing oxides of nitrogen, in order to eliminate the latter by the following overall reduction reactions (15):

$$4\,NH_3 + 4\,NO + O_2 \Longrightarrow 4\,N_2 + 6\,H_2O \quad (1)$$

$$4\,NH_3 + 2\,NO_2 + O_2 \Longrightarrow 3\,N_2 + 6\,H_2O \quad (2)$$

This commercial process, known as selective catalytic reduction (SCR), is operated at large scales, and may be applied to exhausts from gas turbines and coal or petroleum fired power plants or boilers. In one example for exhaust from a chemical plant, a stream containing about 4,000 ppm NOx (combined NO2 and NO) received an addition of similar level of ammonia, passed over a catalyst at 275-300 oC with a residence time of .25 second (space velocity = feed vol rate/reactor vol = 4,000 - 16,000 per hour), and converted more than 90% of the NOx. Importantly, the effluent ammonia level, referred to as the "slip" concentration, was below 10 ppm; thus conversion of the added "contaminant" ammonia was above 99.5% (15).

Ozone Addition to Air

Previous study of PCO air remediation for conversion of aromatics derived from gasoline (as might arise from air stripping of contaminated soil) indicated that xylene and toluene were appreciably more reactive than benzene. As the latter is the only carcinogenic member in common gasoline vapors, its removal was essential, and ozone addition was examined (6) and shown to enhance the benzene removal rate, and thus the quantum efficiency, by an order of magnitude .

Chloro-olefin Addition to Air

Trichloroethylene (TCE) was early identified as a compound with an unusually high quantum yield (16). Nimlos et al (17) proposed that the mechanism for TCE conversion was photoinitiated to provide a chlorine radical based chain reaction. Berman and Dong (18) first disclosed that a mixture of TCE with other, less reactive compounds could enhance the conversion rate of the latter.

Sauer (7a) and Luo (7b) demonstrated that appropriate mixtures of a chlorinated olefin (TCE, PCE, trichloropropene) with toluene could lead to up to 100% conversion of the toluene in a 5 millisecond residence time.

D'Hennezel (7c) recently extended these results to show that TCE enhances conversion of many example pollutants: toluene, ethylbenzene, m-xylene, methyl ethyl ketone (MEK), acetaldehyde, butyraldehyde, methyl-ter-butyl ether (MTBE), methyl acrylate, 1,4 dioxane, and hexane. Thus, many common industrial solvents are susceptible to quantum yield enhancement. Not all are. Compounds exhibiting the more typical mutual rate inhibition when mixed with TCE were acetone, methylene chloride, chloroform and 1,1,1-trichloroethane (7c). Consider the example of PCE enhancement of toluene conversion (7a). Here, the addition of PCE raises the toluene conversion rate from modest values to 100% for an extended period of time. PCE conversion is initially also 100%, but diminishes continually over time. Additionally, toluene deactivation is deferred, but not avoided. This enhancement to achieve 100% conversion for four hours in a 5 millisecond residence time, single pass reactor is an important boost in quantum efficiency for banched aromatics. We note that the branched aromatics toluene and the xylenes are at the top of two EPA priority lists: those for non-carcinogenic emissions and for ozone formation potential.

Further fundamental work is needed using surface science and temperature programming techniques. What is the state of the surface while the presumed chlorine chain reaction is occurring? Can the surface be periodically chlorinated in lieu of continuous addition of chloro-olefins, in order to reduce additive cost and eliminate any "slip" component concentration in the exit stream? Can other additives which do not lead to deactivation be found, e.g. by photolysis of molecular chlorine in the gas phase? Under what geometries would such gas phase photolysis lead to surface chlorination and reaction enhancement, rather than gas phase reaction of chlorine atom products?

Quantum Yield Enhancement: WATER

Quantum yields in liquid phase photocatalytic oxidations are routinely low under conventional, steady state illumination. Values in the range from 0.1% to 5% are common, and Bolton et al (19) have argued that a natural upper limit of about 7% exists for titania because of the natural ratios of active center (hydroxyl radical) formation vs. recombination for the fate of photo-produced holes at the titania surface.

Two circumstances are evident for increasing the quantum yields here. First, when direct hole oxidation of the adsorbed contaminant is possible, quantum yields of approximately 100% are possible, as illustrated by the results of Egerton and King (20a) with neat isopropanol and those of Langford et al (20b) with concentrated alcohol aqueous solutions. Their results indicate that as the chemical activity of water is diminished (20b), or altogether eliminated (20a), the quantum efficiency for liquid phase photocatalysis is of the order of unity. Under this circumstance, harvest of holes for the desired, presumably direct, oxidation proceeds much faster than recombination when the intensity is one solar equivalent or less.

Unfortunately, the characteristic low to very low concentrations of organic contaminants in water appear to yield only low to modest photoefficiencies under steady state illumination.

This circumstance may be avoided using transient illumination, where higher efficiencies are achievable. Szechowski et al (8a) report that with 50 ppm formate solutions using periodic light and dark exposure times, photoefficiencies up to 30-40% are measured when the light exposure time is decreased to .15s with a dark recovery time of 1.45s. When formate is raised to 4000 pm, photoefficiencies averaging 100% are achievable. For maximum effect, the light exposure time must be short: a rapid decline in photoefficiency occurs above .15s. Similarly, the dark time increase causes photoefficiencies to rise, and dark times longer that one second are required to achieve maximum photoefficiencies at either formate concentration. An intriguing observation is that periodic illumination holds greatest promise for dilute solutions. For example, decreasing the light exposure time from near six seconds to .15s increases photoefficiencies about 2.5 fold (from 40 to 100%) at 4,000 ppm formate, but about ten fold at 50 ppm, from about 3% to 25-40%.

Further fundamental work is recommended to discern fully the transient processes involved, determine under what conditions this transient enhancement raises the photoefficiencies for other contaminants, and calculate the corresponding impact on photocatalysis process economics.

Additional Issues

Photocatalysis is a heterogeneous catalytic process, and as such has been demonstrated recently to possess two traditional but undesirable characteristics: catalyst deactivation and production, in certain cases, of unwelcome intermediates.

Gas-Solid Photocatalyst Deactivation

Catalyst deactivation in gas phase treatment has been reported occasionally. Consideration of the number of monolayer equivalents of reactant converted, defined as:

Monolayer Equivalents (MEq) = molecules of reactant converted total surface atoms(estimated) indicates that, for single pass flow reactors, deactivation is ALWAYS observed when the MEq values reach 10-100 (21). In contrast, when recycle reactors are used, deactivation is virtually NEVER reported, for two simple reasons:

- In recycle reactors, concentrations change continuously with time, and a slow deactivation will be masked by the relatively faster changes of concentrations
- Repetition of a given batch experiment, without change of catalyst, should detect catalyst deactivation. Such experiments are rarely conducted and reported.

Such deactivation means that the instantaneous photoefficiency or quantum efficiency is decreasing from the higher initial value to smaller values; eventual achievement of zero activity has been noted with toluene and perchloroethylene conversions(7a). Thus deactivation is subsumed within our theme of efficient photon utilization, and the literature on heterogeneous catalyst deactivation is relevant for new directions.

Our survey in reference (21) embraces results for trichloroethylene (TCE), trichloropropene (TCP), perchloroethylene (PCE), pyridine (P), indole (I), benzene (B), toluene (T), methylbutanol (MB), and dimethyl sulfide (DMS). This widespread evidence of modest operating life of photocatalysts is merely the "welcome" of this emerging discipline to a fact of industrial life: all catalysts have finite lifetimes. Having verified that this ancient characteristic for heterogeneous, thermal catalysts also holds for photocatalysis, it is urgent that we develop regeneration schemes which may, or may not, include further photochemistry. For example, reports exist of restoration of photocatalyst activity upon heating, or illuminating, the catalyst in flowing pure air.

The identities of the deactivation agents resident on these surfaces requires study. Here surface science techniques such as temperature programmed reaction and desorption will be helpful, along with surface analytical techniques such as Auger, ESCA, and EXAFS.

Air Contaminant and Intermediate Levels vs. OSHA Standards

The reaction products in air treatment must be less objectionable than the starting materials. Even with an active and selective catalyst, there is need to more quantitatively evaluate the hazard potential of partly treated air streams. For example, with ethanol conversion over Degussa titania P25, the reaction intermediates include, progressively, acetaldehyde, then acetic acid, and formaldehyde and formic acids. If ethanol to acetaldehyde, and acetaldehyde to acetic acid conversion are each 90 percent complete and leave a stream containing 1 ppm acetic acid and 10 ppm acetaldehyde for every 100 ppm ethanol treated, the relative hazard level of the product stream is about the same as the feed stream because the allowable OSHA limit for each successive reaction intermediate is a factor of 10 below that for the preceding compound in the oxidation sequence! (Table 1). Importantly, such oxidation intermediates are very biodegradable, and a two step process is suggested, further, the environmental lifetime of such intermediates will be modest.

Table 1 Intermediates in Photocatalysis (Ethanol example)(22)

Feed	Intermediates	OSHA PEL(ppm)
Ethanol		1000
	Acetaldehyde	100
	Acetic Acid	10
	Formaldehyde	3
	Formic Acid	5
Sauer (22)		9

Summary

Photocatalytic process economics are centrally tied to the efficient use of photons. The present paper argues that improving the photon efficiencies by known schemes involving 1) process integration, 2) feedstream conditioning and 3) periodic operation and 4) reaction integration provides a set of high opportunity paths to commercial process development. Without a stronger fundamental photochemical focus on this efficiency issue, photochemical remediation of contaminated air and water may remain sparsely applicable and little used.

Photochemical oxidation schemes have been examined long enough that a several problem areas, characteristic of other successful heterogeneous catalysts, have been identified. It is time to carefully address the fundamental photochemistry at work in creating, and perhaps in alleviating as well, these traditional areas involving 1) catalyst deactivation (and regeneration) for air remediation, and 2) catalyst selectivity for desired vs undesired intermediates and final products. In sum, seek photochemical efficiency and honor the history of fundamental research needs in support of commercial catalyst development!

Acknowledgment

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PHOTOSYNTHETIC ANTENNAS AND REACTION CENTERS: CURRENT UNDERSTANDING AND PROSPECTS FOR IMPROVEMENT

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Abstract

A brief introduction to the principles, structures and kinetic processes that take place in natural photosynthetic reaction center complexes is presented. Energy is first collected by an antenna system, and is transferred to a reaction center complex where primary electron transfer takes place. Secondary reactions lead to oxidation of water and reduction of CO_2 in some classes of organisms. Antenna systems are highly regulated to maximize energy collection efficiency while avoiding photodamage. Some areas that are presently not well understood are listed.

Introduction

Nature's most sophisticated and important solar energy storage system is found in photosynthetic organisms, including plants, algae and a variety of types of bacteria. All these organisms utilize sunlight to power cellular processes and ultimately derive most or all of their biomass through chemical reactions driven by light. In this short report I will give an introduction to the basic principles of how natural photosynthetic systems work, including structural, mechanistic and regulatory aspects. This complex subject cannot be adequately explained in such a short space, so the interested reader is referred to some recent books in which various aspects of photosynthesis are explained in more detail (1-3).

Photosynthesis begins when light is absorbed by an antenna pigment. This pigment can be a (bacterio)chlorophyll, carotenoid or bilin (open chain tetrapyrrole) depending on the type of organism. A wide variety of different antenna complexes are found in different photosynthetic systems (4). Antennas permit an organism to increase greatly the absorption cross section for light without having to build an entire reaction center and associated electron transfer system for each pigment, which would be very costly in terms of cellular resources. More details of antenna structure and function are given below. Energy transfer processes that may involve transfers to many intermediate pigments eventually results in the electronic excitation of a closely coupled pair of (bacterio)chlorophyll molecules in the photochemical reaction center (Figure 1). The reaction center is an integral membrane pigment-protein that carries out light-driven electron transfer reactions. The excited (bacterio)chlorophyll molecule transfers an electron to a nearby acceptor molecule, thereby creating an ion pair state consisting of the oxidized chlorophyll and reduced acceptor.

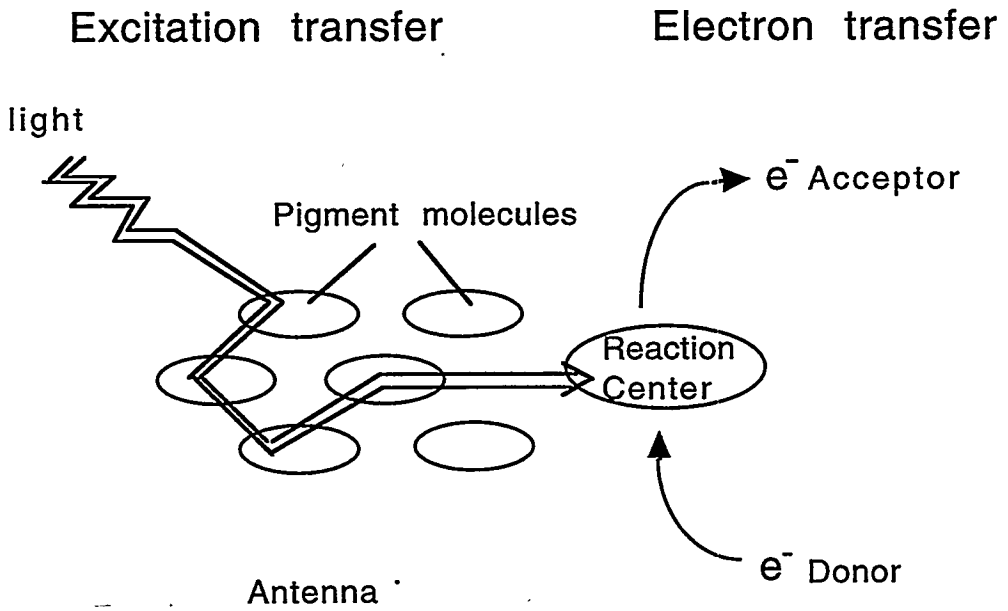


Figure 1. Basic concept of photosynthetic antenna and reaction center function. (Figure courtesy of Judy Zhu).

After the initial electron transfer event, a series of electron transfer reactions takes place that eventually stabilizes the stored energy in forms that can be used by the cell. Some types of photosynthetic organisms have two different reaction center complexes that work together in tandem, with the reduced acceptors of one photoreaction (photosystem 2) serving as the electron donor for the other center (photosystem 1). In these organisms, the eventual electron donor is water, liberating molecular oxygen, and the ultimate electron acceptor is carbon dioxide, which is reduced to sugars. Other types of photosynthetic organisms contain only a single photosystem, which in some cases is more similar to photosystem 2 and in other cases to photosystem 1 of the oxygen-evolving organisms. Oxygen is not produced in any of the naturally occurring single photosystem organisms, which are therefore called anoxygenic. Figure 2 shows comparative electron transfer diagrams of the oxygen evolving and anoxygenic photosystems.

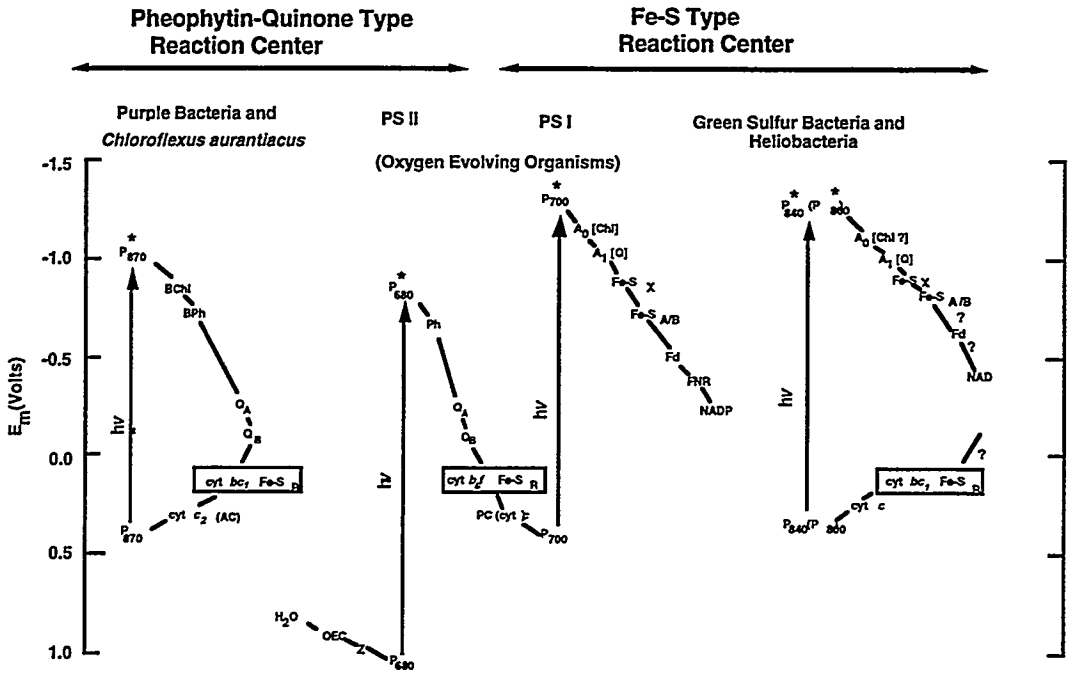


Figure 2. Electron transport diagrams for photosynthetic reaction centers. Vertical arrows indicate energy input by photon absorption, lines indicate preferred electron transfer pathways. Carriers in parentheses indicate alternate species in some organisms. Question marks indicate carriers or electron transfer steps that are likely but have not been unambiguously established. The cytochrome bc_1 and b_6f complexes are boxed, and the details of the electron flow in these complexes are omitted. Figure adapted from reference 5, which includes a complete list of abbreviations.

Reaction Center Structure and Function

The reaction center complexes from the anoxygenic purple photosynthetic bacteria are the best understood of all photosynthetic reaction centers, from both a structural and a functional point of view (1,2). These were the first reaction center complexes to be purified, the first to be studied by

picosecond kinetic methods and the first to have X-ray structures solved. Much of the molecular level understanding of the early events in photosynthesis is based on the information derived from these systems. The structure of the reaction center from *Rhodobacter sphaeroides* is shown in Figure 3.

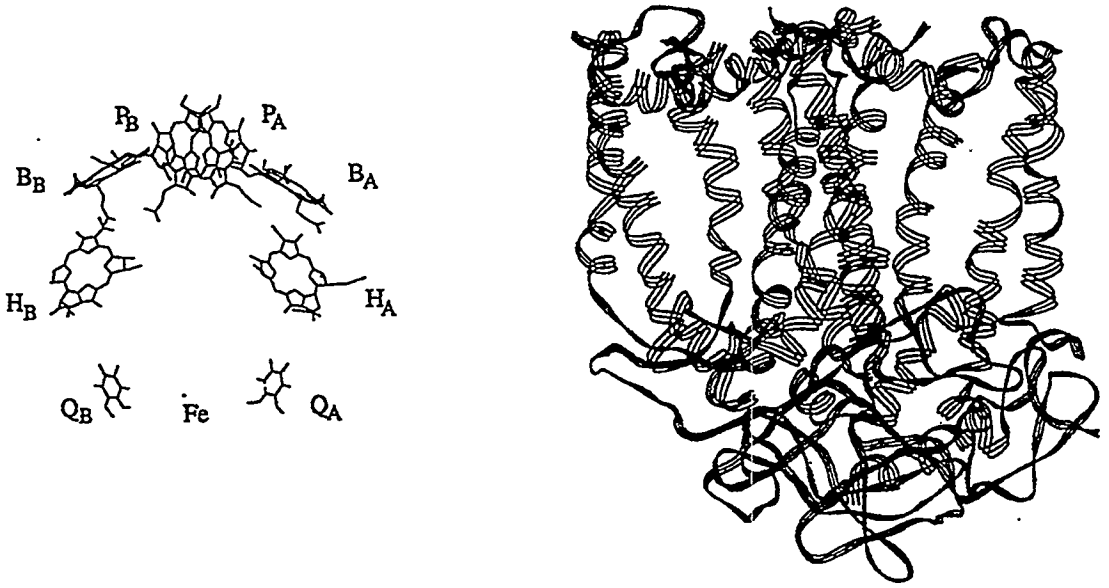


Figure 3. X-ray structure of the reaction center from *Rhodobacter sphaeroides*. Left, cofactors; right protein. The complex is buried in the plasma membrane of the cell, with the helical regions of the protein spanning the lipid bilayer. The cofactor abbreviations are: P, P870 special pair bacteriochlorophyll; B, accessory bacteriochlorophyll; H, bacteriopheophytin; Q, ubiquinone. The A and B subscripts refer to the active and inactive branches of the electron transfer pathways, respectively. (Figure courtesy of James Allen).

The reaction centers from purple photosynthetic bacteria contain a core protein complex consisting of two related yet distinct integral membrane proteins, known as L (Light) and M (Medium). Most also contain a third protein, known as H (Heavy), and some contain a fourth subunit known as C (cytochrome). The C subunit is a four-heme containing *c*-type cytochrome.

In addition to the protein complement, these reaction centers contain several additional cofactors, that are not covalently attached to the protein (Figure 3). These include bacteriochlorophyll *a* (in some cases *b*), the corresponding metal-free bacteriopheophytins, two quinones (either ubiquinone or menaquinone), a non-heme Fe, and in most cases a molecule of carotenoid. The cytochrome subunit contains four heme *c* groups, covalently bound to cysteine residues (not shown in Figure 3).

The reaction center protein forms a scaffolding upon which the cofactors are arranged. The part of the protein that crosses the lipid bilayer is almost purely alpha helical in secondary structure, and contains predominantly nonpolar amino acids, with almost no charged amino acids. There are 11 transmembrane helices, with 5 each from L and M, and one from the H subunit. The L and M

proteins have a pseudo-2 fold axis of symmetry, running approximately perpendicular to the plane of the membrane. The symmetry is broken by the H subunit, which has no symmetry-related counterpart, and also by the fact that the L and M subunits have only about 60% sequence identity.

A large number of different techniques have been utilized on the bacterial reaction center system, including almost every imaginable kind of spectroscopy, as well as a wide range of biochemical and genetic manipulations. Here it is only possible to give a brief summary of some of the results. The technique of picosecond absorbance transient difference spectroscopy has been especially informative with respect to elucidating the pathway of electron flow in these complexes (6). Figure 4 summarizes the photochemical and early secondary reactions that take place in isolated reaction centers. A variety of evidence indicates that the electron transfer pathway and kinetics in isolated reaction centers are not significantly altered from their behavior *in vivo*.

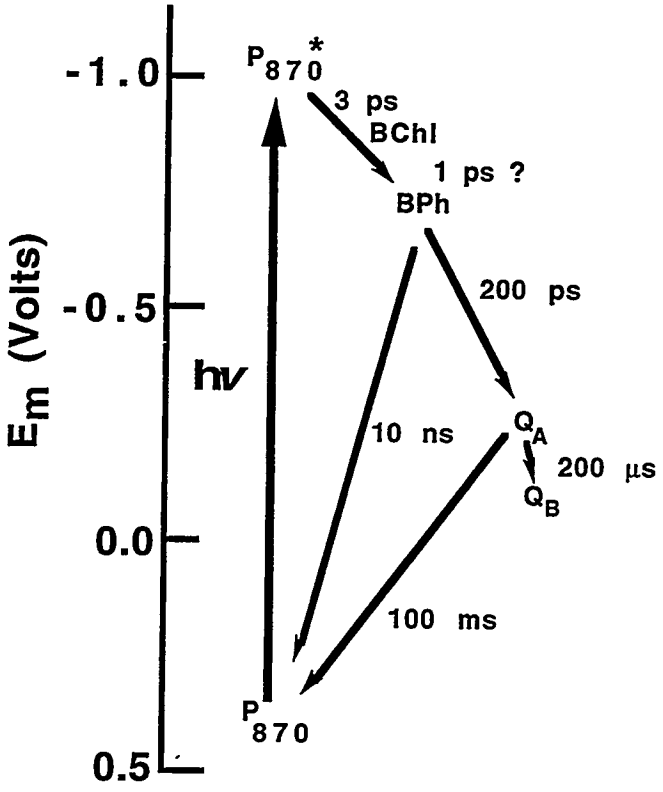


Figure 4. Energy-kinetic diagram for reaction centers from purple photosynthetic bacteria.

Perhaps the most striking aspect of the comparison of the structural and kinetic data on reaction centers is the apparent two-fold symmetry of the structure, contrasted with the clear evidence for asymmetry in the electron transfer pathway. Estimates of the branch ratio for electron transfer down the A branch in Figure 3, compared to the B branch are as high as 200:1. A considerable effort, including analysis of many site-directed mutants as well as detailed theoretical calculations has gone into trying to understand the factors that facilitate electron transfer down the A branch instead of the

B branch. A molecular understanding of this observation has so far been elusive, and forms the basis of much current research.

Another interesting feature of the rate constants shown in Figure 4 is that the rates of recombination processes, in which the electron simply returns from one of the acceptors directly to the oxidized special pair, are invariably a factor of fifty or more slower than are the rate constants for the forward reaction. It is because of this kinetic control of the rates of wasteful processes that the quantum yield for photochemistry is so high. Again, the molecular reasons for this remarkable behavior have proven difficult to elucidate. One of the major factors thought to be involved in the slow recombination rates is the large energy gap involved, placing these reactions in the Marcus inverted region of the rate vs free energy curve. See the contribution by John Miller for more details of this issue.

Other types of photosynthetic bacteria contain reaction center complexes that are structurally quite different from those of the purple bacteria, and our understanding of them is at a much more primitive state. Similarly, structural information on the photosystems from oxygenic organisms is less detailed than that from purple bacteria. It is clear that all photosynthetic reaction centers operate on similar overall principles, so the general lessons learned from the purple bacteria are almost certainly largely applicable to other systems. However, some systems include activities that are not found in the purple bacteria, such as oxygen evolution by photosystem 2. Therefore, study of more than one type of organism is necessary to understand the wide scope of processes that are carried out by photosynthetic reaction centers.

Function and Regulation of Antenna Systems

The vast majority of the pigments in a photosynthetic organism are not chemically active, but function primarily as an antenna (1,4). The photosynthetic antenna system is organized to collect and deliver excited state energy by means of excitation transfer to the reaction center complexes where photochemistry takes place. The antenna system increases the effective cross section of photon absorption by increasing the number of pigments associated with each photochemical complex. The intensity of sunlight is sufficiently dilute so that any given chlorophyll molecule only absorbs at most a few photons per second. By incorporating many pigments into a single unit, the biosynthetically expensive reaction center and electron transport chain can be used to maximum efficiency. A remarkable variety of antenna complexes have been identified from various classes of photosynthetic organisms. There seems to be little doubt that there have been multiple evolutionary origins of antenna complexes, as there is no common structural theme evident.

Excitation transfer must be fast enough to deliver excitations to the photochemical reaction center and have them trapped in a time short compared to the excited state lifetime in the absence of trapping. Excited state lifetimes of isolated antenna complexes, where the reaction centers have been removed, are typically in the 1-5 ns range. Observed excited state lifetimes of systems where antennas are connected to reaction centers are generally on the order of a few tens of picoseconds,

which is sufficiently fast so that under physiological conditions almost all the energy is trapped by photochemistry.

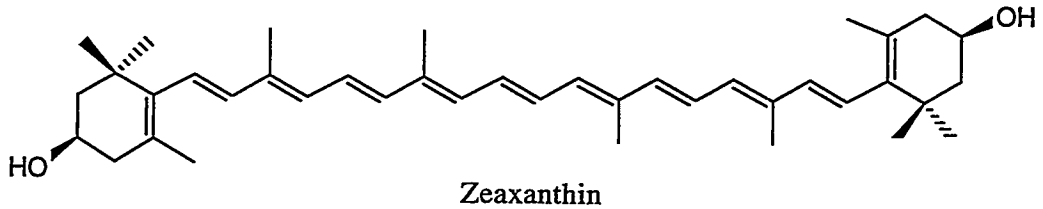
Antenna systems are often viewed as being "on" all the time, with the regulation of photosynthesis in response to different conditions taking place primarily in the reaction centers and carbon metabolism enzymes. Clearly, this is not the case, and the modern view is of a much more actively regulated system at all stages of energy storage. The advantages of "directional signals" or "volume controls" to regulate either the distribution between the photosystems or the number of excitations delivered by the entire antenna network are easy to appreciate.

One of the most interesting and important of these regulatory mechanisms is the phenomenon of "nonphotochemical quenching" (q_N) of chlorophyll excited states in chloroplasts (7). During periods of high irradiance such as midday, or under certain stress conditions, a substantial fraction of the excited state energy is dissipated by quenching before it is ever transferred to the reaction center. The basic idea is that it is much easier and safer for cells to dispose of this energy before it initiates the photochemical processes in reaction centers than it is for them to try to repair the substantial photooxidative damage that can result from excess light. This process is now thought to be a major regulatory mechanism and understanding it is likely to have great economic significance.

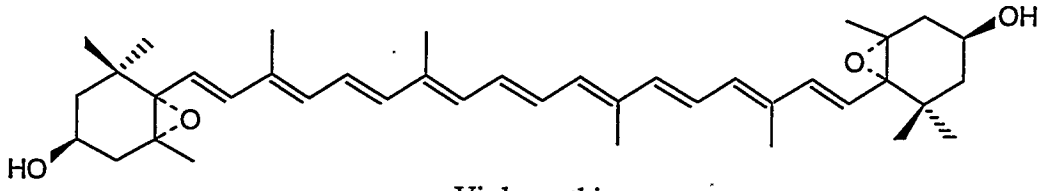
Considerable evidence indicates that a cycle involving carotenoids known as xanthophylls plays a role in this regulation, with zeaxanthin associated with the quenched state and violaxanthin associated with the nonquenched state (Figure 5) (8). Enzymes interconvert these carotenoids in response to energetic signals generated in the chloroplast. The chemical mechanism of the quenching effect is not yet understood in molecular detail. One proposal under investigation is that the zeaxanthin molecule with its more extensive conjugation has a lower excited state energy than does violaxanthin. The excited state energies are proposed to be such that violaxanthin lies above chlorophyll and therefore acts as an energy donor while zeaxanthin lies below chlorophyll and therefore acts as an excited state quencher (9). Other factors are also known to be important, including the state of aggregation of the antenna complex and the pH of the interior lumen region of the thylakoid membrane (10). The chlorophyll *a/b*-containing antenna complex known as LHC II is thought to be the site of much of this quenching reaction. This complex is well characterized structurally (11). While the linkage of the quenched state to the presence of zeaxanthin in the membrane is clear, it is mostly based on evidence showing that the two are correlated, rather than an unambiguous cause and effect relationship.

Future Challenges

There are many fundamental unsolved questions relating to the mechanism of energy storage by natural photosynthesis. Certain of these questions directly relate to the effort to develop artificial photochemically based systems for solar energy storage, in which water is oxidized to molecular oxygen, along with either hydrogen production or CO_2 reduction. Chief among these is developing a deep understanding of the physical principles by which all natural photosynthetic systems avoid



Zeaxanthin



Violaxanthin

Figure 5. Molecular structures of zeaxanthin and violaxanthin.

the wasteful recombination reactions involving early radical ion pair intermediates. A second important area includes the elucidation of the details of the reaction center structure and chemical mechanism of water oxidation by photosystem 2. A third area involves structure and function of photosystem 1, including how the strongly reducing early electron acceptors avoid autooxidation by oxygen (12). Finally, a broad area that is presently very poorly understood includes the dynamic regulation of natural antenna systems so as to maximize energy collection efficiency under a variety of conditions while at the same time avoiding harmful overexcitation and subsequent damage. Ultimately, an understanding of these principles that underlie natural photosynthesis should point the way to the development of efficient, robust artificial systems for solar energy storage.

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ELECTRON, PHOTONS, AND MOLECULES: STORING ENERGY FROM LIGHT

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Abstract

Molecular charge separation has important potential for photochemical energy storage. Its efficiency can be enhanced by principals which maximize the rates of the electron transfer steps which separate charge and minimize those which recombine high-energy charge pairs to lose stored energy. Dramatic scientific progress in understanding these principals has occurred since the founding of DOE and its predecessor agency ERDA. While additional knowledge in needed in broad areas of molecular electron transfer, some key areas of knowledge hold particular promise for the possibility of moving this area from science toward technology capable of contributing to the nation's energy economy.

Introduction

Semiconductors such as silicon and both natural and synthetic molecular arrays store energy by light-driven charge separation. While semiconductor solar technology is far ahead, molecular charge separation holds great promise for energy storage. Principles for optimizing efficiency of charge separation are discussed herein. A view of what needs further understanding will follow from a retrospective look at the dramatic progress since the creation of DOE and its predecessor (ERDA) in the 1970s.

The Early 70s

In the early 1970s it was possible to make electricity from semiconductor solar cells. Chlorophyll was known to capture energy and store it in the form of sugars and it was thought that electron transfer might be involved in the process, but it was not yet known that electron transfer did in fact provide the essential mechanism for conversion of light energy into stored chemical energy. There were no man-made molecular devices to perform such energy capture by charge separation and not even conceptions for such devices. Most of the underlying principles for their operation were yet to be discovered.

The electron transfer theory of Marcus (1,2) described an energy specificity which we now know can enhance energy storage. The theory predicted a relationship between kinetics and thermodynamics in which electron transfer rates were expected to be maximized for a moderate free energy change (ÎG°), but to actually decrease at larger energies. The decrease in rate with decreasing energy known as the "inverted region" was found not to occur in the famous experiments of Rehm and Weller (3) as shown in Figure 1.

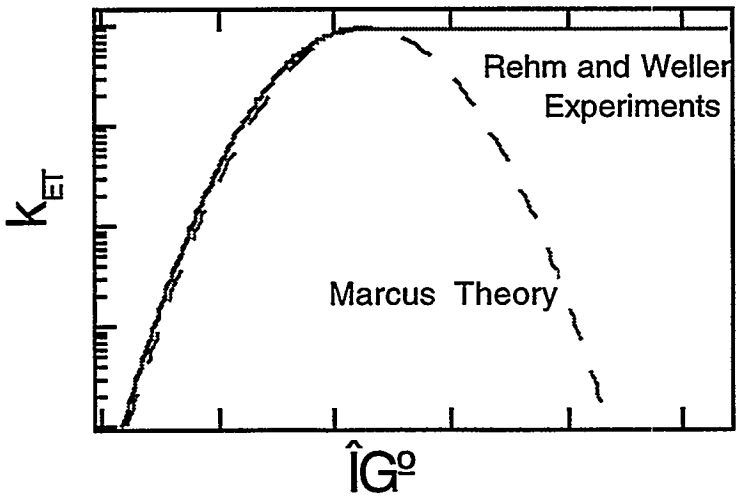


Figure 1. The Marcus theory (dashed line) predicted that electron transfer rates would decrease with increasing free energy change, but experiments by Rehm and Weller (solid line) found no such decrease to occur.

There were also reports of long-distance electron transfer (4), but they were viewed with some skepticism. Most chemists believed that molecules had to come in contact in order to transfer electrons. Photochemical solar energy schemes were conceived based on mixtures of components and fluid solutions and organization of components in structures such as micelles. Those schemes show little promise even to this day.

Energy Storage by Molecular Charge Separation

Since those early days we have found that energy can be stored by electron transfer reactions in a graded set of molecules arranged in a fixed way in space as shown in the energy-level diagram of Figure 2.

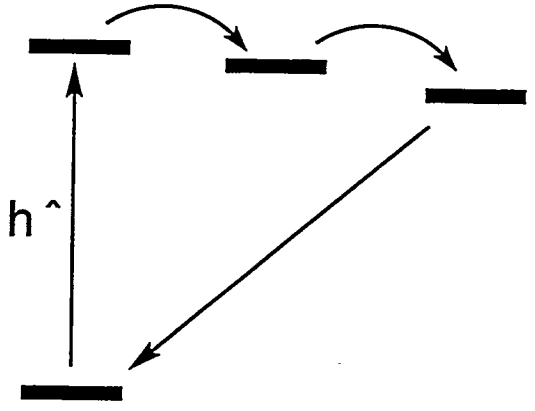


Figure 2. Light absorption by the molecule on the left leads to transfer in the graded set of energy levels to a second and then a third molecule.

Experiment and theory have shown that electron transfer rates are described as a product of the square of an electronic coupling term (V) and a Franck-Condon weighted density of states. Electronic coupling gives the rates a strong distance dependence, which is sensitive to issues such as hole transfer vs. electron transfer, β vs. π material in the region between the donors and acceptors, and orientation dependence with the possibility of cancellation by symmetry. The Franck-Condon weighted density of states (FCWD) contains the dependence of the rates upon free energy, temperature, and polarity. In the charge separation scheme of Figure 2, it is desired to manipulate these factors to make the forward electron transfer rates which separate charge fast, while slowing the back electron transfer rates which return the electron to dissipate the stored energy. It is desired to do this while driving the forward steps by only small amounts of free energy to retain a large fraction of the free energy from the initial photon.

DOE-supported experiments showed that when the distances between donors and acceptors were fixed, the inverted region did indeed exist (5,6) but the shape of the rate vs. free energy curve departed somewhat from that predicted by the classical Marcus theory due to quantum mechanical effects from high-frequency molecular vibrations (Figure 3a). The experiments clearly supported

the theoretical concept that the rate was maximized at a reorganization energy, ¬, which was the sum of two parts, $¬_s$ and $¬_v$, the solvent and internal vibrational reorganization energies. Experiments further showed that the solvent reorganization energy that could be manipulated by changes in solvent polarity produced dramatic effects on electron transfer rates as shown in Figure 3b.

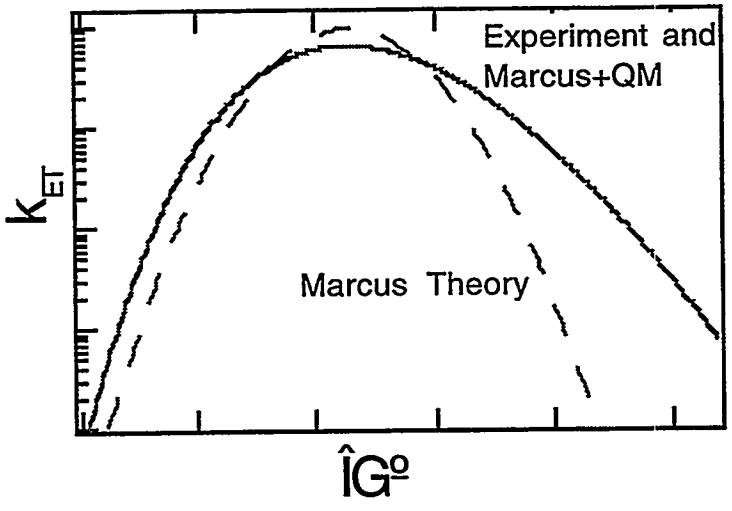


Figure 3a. The inverted region found for fixed distance electron transfer between molecules differ slightly from the predictions of the classical Marcus theory (dashed line).

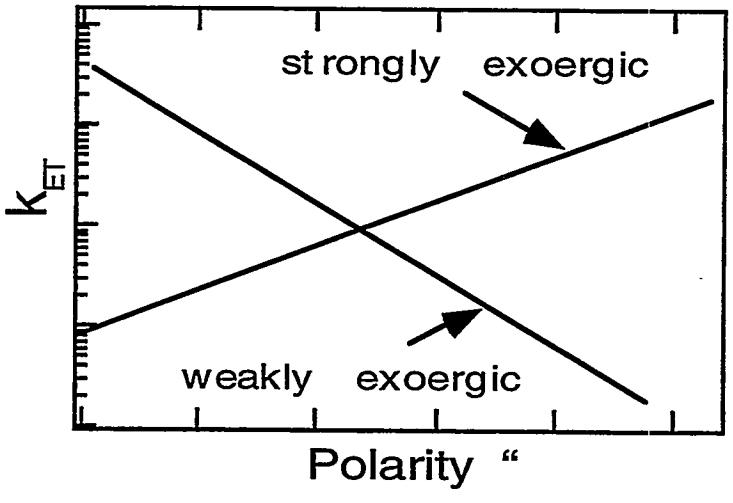


Figure 3b. Electron transfer rates as a function of polarity for a weakly exoergic (solid line) and a strongly exoergic (dashed) electron transfer reactions having the same distance and electronic couplings.

These results are obtained most quantitatively in experiments using picosecond pulses from linear accelerators, where the effect of one variable, such as polarity, can be studied while keeping the others fixed, but they are also confirmed in experiments involving photoexcited charge separation. It is clear then that the inverted region may be used to enhance the efficiency of charge separation and that this is done best when reorganization energy is minimized. Contrary to many early opinions that a highly polar environment is best for charge separation, it is now understood that we should run energy storage reactions in oil or silicon, not water. What is not as clear is how to reduce the internal reorganization energies due to the molecules themselves. Research is needed on this question and on how to promote low reorganization energies of medium when it may not be possible to construct the medium out of completely non polar material. An important challenge is how to minimize the total reorganization energy. A related question is: Are very low reorganization energies inferred from some experiments (7) on photosynthetic reaction centers correct? And if so, how is this achieved?

To efficiently store energy by charge separation using the scheme in Figure 2, it is also necessary to know how far apart to place the donor and acceptor groups. Great progress has been made in understanding the dependence of electron transfer rates on distance (5,8-12). It is understood that the exponential decrease of rates is most rapid through a vacuum and that long-distance rates are greatly enhanced when molecular material is present between the donor and acceptor. Further enhancement occurs if there is a connected series of bonds between the donor and acceptors. The electronic couplings may be further affected by the conformations and connectedness of these bonds. Some of the experiments have shown that greatly increased electronic couplings can occur when conjugated π bonds lie between the donor and acceptor group (13-19) The results to date would indicate the possibility that π materials between donors and acceptors could promote rapid electron transfer to very long distances, but this possibility is yet to be demonstrated and its use in promoting efficient charge separation to long distances needs to be well understood.

Another aspect of electronic couplings is the dependence on the tunneling barrier heights which might be expected to be used to greatly enhance the forward charge separation rate (k_f) relative to the reverse back reaction rate (k_r). Figure 4 shows a simplified scheme in which an intermediate electronic state lying between the photoexcited donor and the acceptor provides a small barrier height forward for superexchange in forward electron transfer. But because the acceptor energy level lies lower the barrier height for electronic coupling in reverse electron transfer is higher. It has not yet been demonstrated that this barrier height effect can influence the ratio (k_f/k_r) and an adequate theory does not exist to understand the limits of this effect.

Molecular orientation can also control electron transfer rates (20-23), because the absorption of the photon alters the symmetry of the electronic wave function as schematically illustrated in Figure 5. The orientation which is optimal for electron transfer from the excited state to an acceptor is different for the orientation optimal for energy-wasting back reactions. Experiments by Zimmt (24,25) and McLendon (26) indicate the possibility of substantial orientation effects in electron transfer, but these experiments are not conclusive. Experiments and theory are needed to adequately

delineate the limits of this effect and to provide an understanding of whether it could have an impact on real charge separation systems.

Assemblies of Molecules

The effects of distance and energy outlined above have been used to synthesize covalently linked assemblies of electron donors and acceptors, particularly by Gust and Moore (27,28) and by Wasielewski and co-workers (29,30). These molecular assemblies duplicate some of the functions of the reaction center that store energy by separation of charge in photosynthetic bacteria and plants. These molecules, which store a large fraction of the energy of the photon with large quantum efficiency, represent stunning achievements compared to our complete lack of knowledge about such processes two decades ago. Such molecules are expensive to make and research is needed to find whether inexpensive alternatives can be created and to find ways to couple this energy storage by charge separation into the creation of fuels.

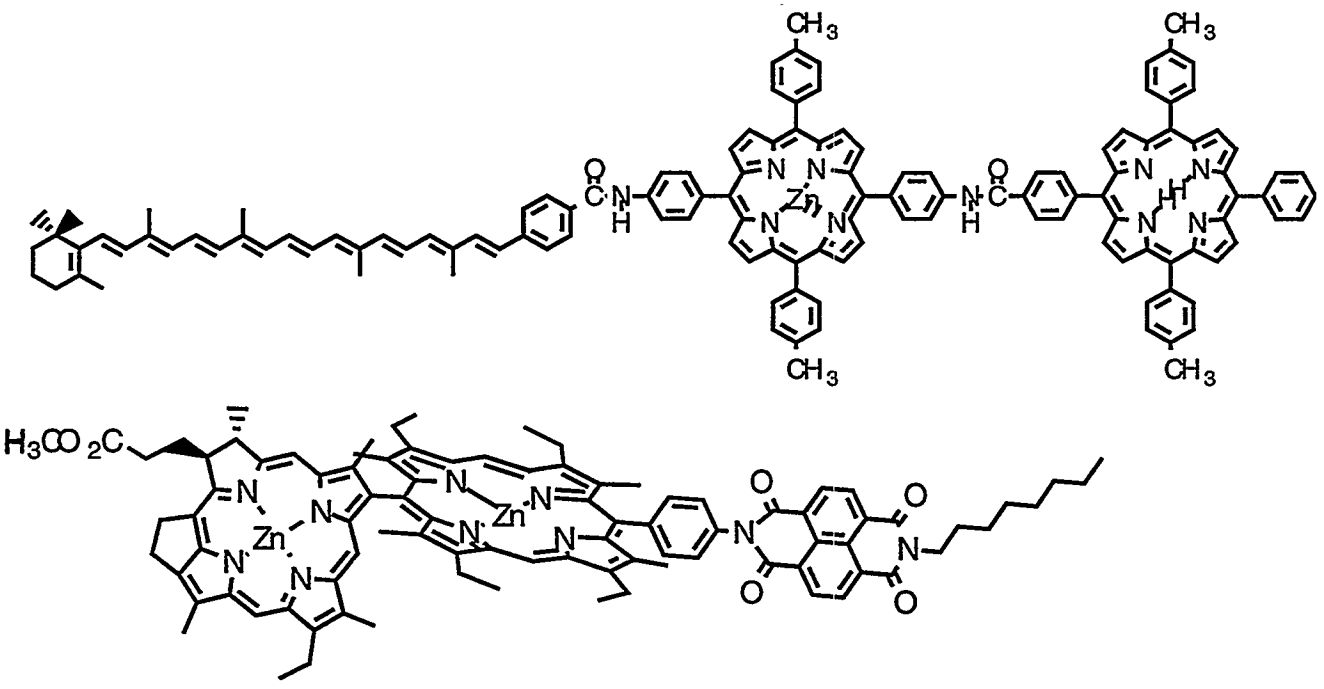


Figure 4. Molecular assemblies of Gust (28,31) and Wasielewski that are capable of efficient light-driven energy storage in the form of separated charges.

Molecular cages present a new and almost completely unexplored approach to gaining energy specificity and possibly electronic control for charge separation reactions. Recent work by Deshayes found energy specificity in triplet-triplet excitation transfer when the triplet energy donor was enclosed in a hemicarcerand. Research is needed to determine whether such energy specificity can also occur for electron transfer and whether this specificity might revive older ideas of electron transfer in homogeneous solutions as a basis for energy storage.

Silicon or Molecules?

One possible answer to the question of whether semiconductors or molecules will provide better technology for solar energy conversion is not either/or but both/and. Examples of the semiconductors and molecules approach are provided in Grätzel's presentation in this meeting and in the extensive studies discussed here about photoelectrochemical cells. If the best technology may be a composite, an important question is: Are there additional new ways to combine molecules and semiconductors?

2n Electrons

Although tremendous progress has been made in understanding how to capture the energy of photons by charge separation, this is single-electron photochemistry. The largest challenge in producing fuels is how to drive 2n-electron photochemistry to create stable molecular species, which is a major theme of the discussion by Dr. Fujita in this workshop, and is investigated by Nocera (32). This question has been the province of catalysis, often at metal or other solid state surfaces. We need to learn more about molecular catalysis for light-driven redox chemistry, and we need to learn how this is done by plants. A related question is the need to use low-energy solar photons to drive high-energy reactions that may require the combination from two or more photons. This might be done by C-schemes, as is the case in plant photosynthesis.

Perspectives

Table 1 summarizes in a list some principles that can contribute efficient chemical energy storage. For some principles there exist experimental verification, theoretical understanding, and a large number of experiments, whereas for others substantial additional knowledge is needed.

Finally, we single out the list of topics where there is a particular need for research to provide new understandings in molecular energy storage:

1. How can we obtain very small total reorganization energies?
2. How can we transfer electrons over very large distances?
3. Can orientation and symmetry be useful in discriminating against back reactions while allowing forward reactions?
4. Can we use tunneling barrier heights to promote forward reactions relative to back reactions?
5. Can we develop further strategies to combine two or more photons of modest energies to drive high energy redox processes?
6. Can we thoroughly understand molecular charge separation devices that work, such as photosynthetic reaction centers, molecular arrays and the Grätzel cell?
7. Can new constructs such as molecular cages promote efficient charge separation?
8. How do we efficiently drive processes which separate 2n electrons?

Strategies Using Effects of:	Exper-iment	Many Examp.	Theory	Promotes Charge Separation
Inverted Region	▬	▬	▬	◖
Polarity	◖	◖	▬	◖
Medium Relaxation	◖	◖	◖	
exp(-∫R)	▬	▬	◖	◖
Barrier Heights, ∫ » ln(B)	◖		◖	
Through-Bond, ∏ Enhancements	◖	◖	◖	◖
Interference, Orientation,	◖	◖	◖	
Spin Dynamics	▬	▬	▬	▬
Coherent Fwd., Incoherent Back	◖		◖	
Molecular Cages			◖	
Self Decoupling	◖	▬	◖	◖
Electrostatic Effects	▬	▬	▬	▬

Table 1. Strategies for promoting efficient energy storage by light-driven charge separation. Indication is given of how well each concept has been demonstrated experimentally, whether there are many experimental examples, how well the concept is described by theory and whether it is actually known to promote efficiency of charge separation.

Acknowledgments

Thanks to a number of colleges who contributed thoughts to this presentation: Carol Creutz, Kurt Deshayes, Devens Gust, Nate Lewis, Marshall Newton, Dani Meisel, Arthur Nozik, Jim Norris, Piot Piotrowiak, Norman Sutin, Marion Thurnauer, Dave Tiede, Matt Zimmt, Mike Wasielewski. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, under Contract No. W-31-109-ENG-38.

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U.S. DOE Office of Energy Efficiency and Renewable Energy Program Overviews

PHOTOVOLTAIC TECHNOLOGY AND APPLICATIONS: OVERVIEW FOR THE WORKSHOP ON PHOTOCHEMISTRY RESEARCH OPPORTUNITIES

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The business surrounding photovoltaic energy conversion for terrestrial applications has changed dramatically in the last several years. It is now a business that makes money. Industry is responding with manufacturing capacity expansions, and planned expansions, that will triple U.S. annual output within the next eighteen months. The majority of this product is exported (70%) where it is proven to be a cost competitive alternative. This industry provides experience in manufacturing and reliability in fielded systems that will serve as the basis for extrapolating growth to larger-scale installations and utility systems. The largest part of the National Photovoltaic Program budget supports assisting industry in advancing manufacturing technology and stimulating applications to reduce cost and expand the evolving industry.

A growing segment of society looks to photovoltaics as an alternative that may be needed to replace conventional electric generating capacity. While still the focus of much debate, the body of evidence of global warming appears to be growing. The use of fossil fuels may contribute to global warming due to changes in the optical properties of the atmosphere resulting from increased concentration of CO_2. Between now and the year 2000, world wide demand for new electric generating capacity is projected to grow by 600 GW -- nearly as much as the existing capacity in the US today. Two thirds of this expansion will address needs of less developed countries. Today, China ranks third in emission of greenhouse gases, although its per capita electric energy consumption is not in the top 50. The need to provide electric power in developing countries may be the dominant environmental and social issue for the next decade. Longer term, a report by Shell Oil Company projects that by 2040 more than one half of new energy capacity will need to be supplied by renewable energy sources. The grand challenge for photovoltaics is to make the technology economically competitive for large scale electric power generation before real or perceived evidence of environmental damage from conventional sources dictates its use at economically disruptive costs.

In 1995, the photovoltaic (PV) power industry produced new systems that generate a combined peak output of 81 megawatts. Most of the individual systems are less than a kilowatt and power applications such as water pumping, communications, cathodic protection, refrigeration and lighting. System costs are in the range of $6 to $10 per peak watt for many U.S. installations. Assuming the systems are sufficiently durable to perform for 30 years, the cost of electricity produced is $0.25 to $0.60 per kilowatt-hour. The market in these types of applications is growing by about 15% per year. The growth in production volume along with supporting research, development and manufacturing technology from the Federal program are driving manufacturing cost reductions of

10% to 20% per year. Systems prices are coming down by about 5% per year. The cost of module contributes only about half of the total system price, but price reductions for modules account for most of the system price reduction. The combination of these trends has placed the industry at the break even point, where some companies are now reporting profits.

Current costs are quite close to meeting the requirements for a wide range of new, larger scale applications. PV modules are replacing architectural glass in some buildings to generate tens of kilowatts of power, reducing peak demand from the utility sources. Utilities will use the distributed generation for substation support and to delay increasing capacity of transmission lines. The growth rate will warrant building much large-scale factories for photovoltaic module manufacturing using higher throughput processes, such as rapid thermal processing and high rate laser patterning, for module production steps and a higher level of automation with concomitant demand for in-line monitors and control. As this product cycle matures, PV generated electricity costs and the favorable match between time-of-day capacity and peak customer demand should make the technology competitive with gas turbines for power generation distributed within the utility grid.

Most modules are manufactured from wafers of silicon. These wafers are either sliced from Czochralski or cast ingots, laser cut from a ribbon or recycled from integrated circuit industry rejects. The photovoltaic industry consumes only about 10% of the world-wide consumption of silicon used in electronic products. This situation, combined with the notorious cycles in the integrated circuit industry, forces the PV industry to dependence on surplus and scrap feedstock. The industry must be flexible in its ability to use a wide range of source quality. The wafers typically have high levels of dislocations and dissolved and precipitated impurities. Research focuses on processes that employ point defects to relocate impurities, passivate electronically active defects and modify crystal defects to more benign configurations.

Thin film technologies can provide a new regime of photovoltaic products. Reduced material consumption, continuous in-line production processes and potentially simplified packaging can lead to significant cost reductions. The electro-optic properties of conventional thin-film semiconductors will require device designs that optimize absorption in electrically useful regions of the solar cell. Such designs will require coupling electronic models with optical model incorporating interference effects and heterostructures of dissimilar materials. Capturing the benefits of thin-film technology requires that simple processes be developed that produce large-areas of materials with superior electronic properties.

Increasing the dimension of solar cells reduces processing cost, but usually demands a penalty in increased losses due to lateral resistance. This trade-off drives the interest in improving control of semiconductor alloys to form multiple-junction cell partners or higher band gap devices. The trade-off can also be addressed by development of transparent conducting oxides that can provide both high transparency and high carrier mobilities.

The dominance of wafered silicon technology in today's PV market is attributable to the benefit of the infrastructure supporting other electronic and photonic applications. An infrastructure of

materials, expertise and equipment manufacturers is growing in the U.S. around amorphous silicon for thin-film transistors. For several of the promising materials, cadmium telluride and copper indium diselenide, the PV technologies seem relatively unique. The lack of direct analogous manufacturing processes presents a major hurdle to rapid commercialization. Capital costs for one-of-a-kind equipment may prove prohibitive. A challenge will be to network into many different industries that may use comparable technologies in some steps, for example optics manufacturing for deposition of dielectric coatings or source materials purification.

The October issue of Photonics Spectra includes an editorial comment that describes a recent survey conducted among leading Japanese scientists and engineers regarding what they thought should be the priority goals in electronics and photonics over the next ten years. By a wide margin, they selected development of low-cost photovoltaic systems. The Japanese government supports a program about twice the size of the U.S. effort. Since their fuels are completely imported, a major portion of their program is directed toward development of technology compatible with Japan's highly urban population and limited availability of area for installing solar collectors. These conditions drive the balance in their funding toward high efficiency technologies. Most of the Japanese PV program is seeking a 50% increase in efficiency from silicon technology. Longer term research is seeking technologies that might achieve 30% conversion efficiencies. The remaining portion of their program investigates the thin-film technologies for the large anticipated export markets to the developing countries. Similarly, European interest and support for developing PV systems is greater than in the U.S. With the current emphasis of reducing Federal spending, the PV community in the U.S. can only meet the foreign competition by seeking out partners in other research or product areas to leverage the limited resources in a network built on common manufacturing technologies and research interests. Workshops such at this are essential for the formation of these important linkages.

PHOTOCHEMISTRY RESEARCH AT NREL

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Abstract

Photochemistry research team at NREL conducts research and development work in all R&D areas, basic, applied, demonstration and transfer to commercialization. Basic research includes core PCO R&D and catalysts work as well as conducting research into new photochemistry areas such as photoinduced adsorption and high temperature solar PCO. Applied research work consists of remediation of chloroethylenes in gas phase, gas phase solar photoreactor development, and application research including indoor air quality, hybrid biological/PCO processes and more. We are demonstrating the PCO treatment technology in the gas phase with SEMATECH through CRADA work and remediation of organics in aqueous phase through the Solarchem Environmental Systems. We are working with IT through a CRADA to transfer the PCO gas phase remediation technology to IT to commercialize this promising technology. Photochemistry research conducted at NREL spans the R&D spectrum from basic research through technology demonstration with the goal of technology commercialization.

History of NREL photocatalytic oxidation (PCO) R&D

Photochemistry research has been sponsored in large part by the DOE Office of Industrial Technologies. This year we also have major funding from the Department of Defense through the U.S. Army Corps of Engineers Research Laboratory in Champagne, Illinois. The PCO research spans the classic R&D spectrum from basic, applied, demonstration and commercialization.

PCO R&D was initially funded in 1989 by DOE. PCO in aqueous phase, catalyst, slurry troughs, and concentrated sun light were the first areas of research. A field pilot test was conducted in 1991 at Lawrence Livermore. This field pilot test resulted in moving from a solar concentrator system to one sun research and research began on supported catalyst. A second field test was conducted at Tyndall Air Force Base using a slurry system. The results of the Tyndall AFB field test moved the PCO research from the aqueous phase into gas-phase research. The data gathered from the field test indicated that air stripping the volatile organic pollutant compounds (VOCs) was economically more cost effective and more efficient. In 1993 a CRADA was signed with International Technology Corporation (IT) for the purpose of conducting cooperative research and development in the area of commercialization of PCO remediation technology. In 1994 a CRADA was signed with SEMATECH to conduct cooperative research and development in the process semiconductor industry using PCO technology. Other industrial collaboration partners are International Fabricare Institute and American Bakers Association.

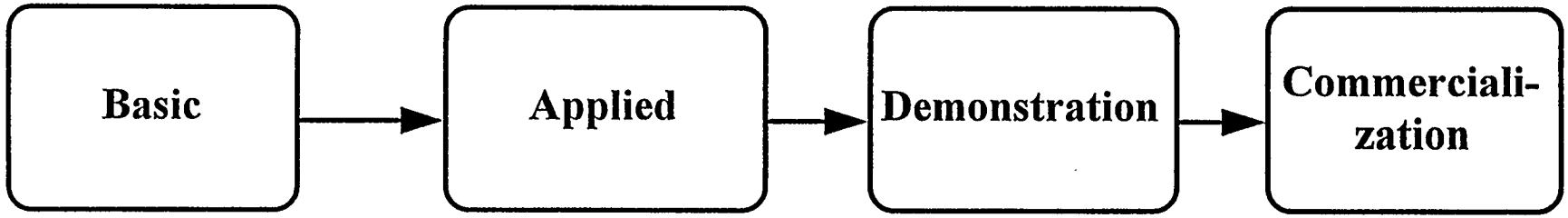
Core PCO R&D

(Basic)

Core PCO R&D currently being conducted is focused on improving understanding of gas phase PCO process and identifying the scientific basis for TiO_2 activity. In the area of improving the understanding of gas phase PCO process the goal is to characterize and understanding the gas phase PCO process to improve efficiency. Research is being conducted in the kinetics of decomposition of oxygenated organic compounds, humidity effects, light intensity effects adsorption and characterization of catalyst surface chemistry.

The kinetics of decomposition is the measuring the rates of destruction and formation rates of intermediates and products of selected compounds. Kinetic parameters of the reaction are determined by modeling the experimental data. Research work includes efforts to understand the humidity effects to determine operating parameters for optimal performance of PCO reactors. Investigation of light intensity effects includes work on the effect of light intensity upon the overall chemistry, destruction of the starting material, and formation of intermediates and products. Light intensity effects of PCO chain reactions and development of a comprehensive model for packed bed reactors are also areas of research. The final two areas of gas phase PCO process research are adsorption and characterization of catalyst surface chemistry. These areas of research will assist in characterizing and understanding the gas phase PCO process and improving efficiency.

PCO R&D Technology Spectrum



- Improve understanding of gas-phase PCO
- Catalyst development

- Chloroethylenes gas-phase

- Scientific basis for TiO_2 activity

<u>New R&D</u>

- Photoinduced adsorption
- High temperature solar PCO

- Improve treatment of chloroethylene
- Gas-phase solar reactor design
- Gas-phase PCO for IOF applications
- Indoor air quality
- Biological/PCO
- Matrix isolation
- Ultrapure water
- Water disinfection

- Semiconductor industry air emissions
- Solar remediation of organics in aqueous-phase

Figure 1

Figure 1. PCO R&D Technology Spectrum.

Core PCO research is being conducted to determine the scientific basis for TiO_2 activity. We are working on redox kinetics of titanium dioxide to develop a phenomenological model and describe the kinetics of PCO and reduction and the activity of TiO_2 in terms of light intensity, reactant concentration and catalyst characteristics. In May 1995 a CRADA was signed with DuPont to conduct cooperative research and development in these areas. This work is done primarily by Sandia National Laboratory. The results of this research will support the development of a photo activity database and a photoredox model for the behavior of aqueous suspensions of TiO_2 (P25 grade).

Catalyst
(Basic and Applied)

Extensive research is being conducted on catalyst performance and catalyst development. We are developing new photocatalytic materials for environmental applications for use in both gas and aqueous phase applications. A portfolio of catalyst activity for specific applications through treatability evaluations is under development. The aqueous phase treatability includes both organic metallic pollution in water.

Remediation of Chloroethylenes in Gas Phase
(Applied)

The applied section of the R&D spectrum is remediation of chloroethylenes in gas phase. The IT CRADA objectives are to develop PCO technology as an air pollution control method for VOCs. Industrial processes are investigated, including process equipment vents, building exhaust vents, vents from environmental remediation processes, and fugitive emissions from regulated sources for potential commercial applications. The R&D emphasis of this is to improve process efficiency and decrease cost. IT's first pilot system undergoing modification is lamp based and skid mounted. A field test is planned in Phoenix, Arizona, at a Superfund site this summer.

PCO treatment of air emissions from the Semiconductor Industry
(Demonstration)

The SEMATECH CRADA objectives include developing PCO for application to the air emissions from the semiconductor industry. A pilot test was conducted during January-February 1996 at a Hewlett-Packard (HP) plant, located in Fort Collins, Colorado. The HP pilot test consisted of process air streams at the semiconductor manufacturing plant. The objectives of the HP field test were: determine if PCO technology can obtain >95% destruction levels under field conditions, evaluate catalyst lifetime under field conditions, test the process on emission streams that contain compounds that were not evaluated in the laboratory. The final results will be used to evaluate whether PCO technology should be pursued to a pilot demonstration.

The pilot test was not a simple undertaking; it consisted of treating a live process air stream, real time at the site. The cart contains the PCO treatment system and analytical equipment. The system is lamp driven and has been modified for use in this pilot. The flow schematic is an

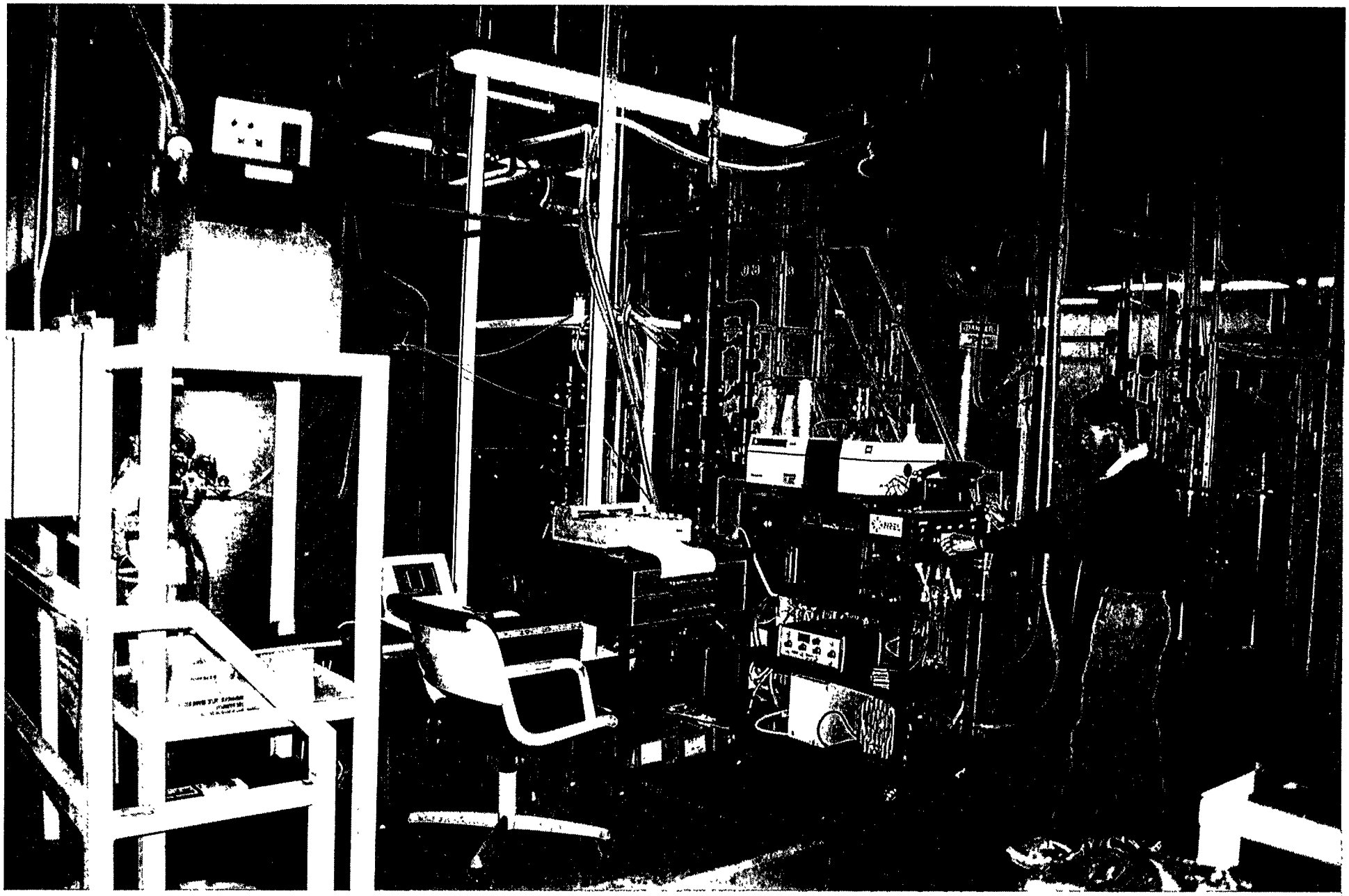
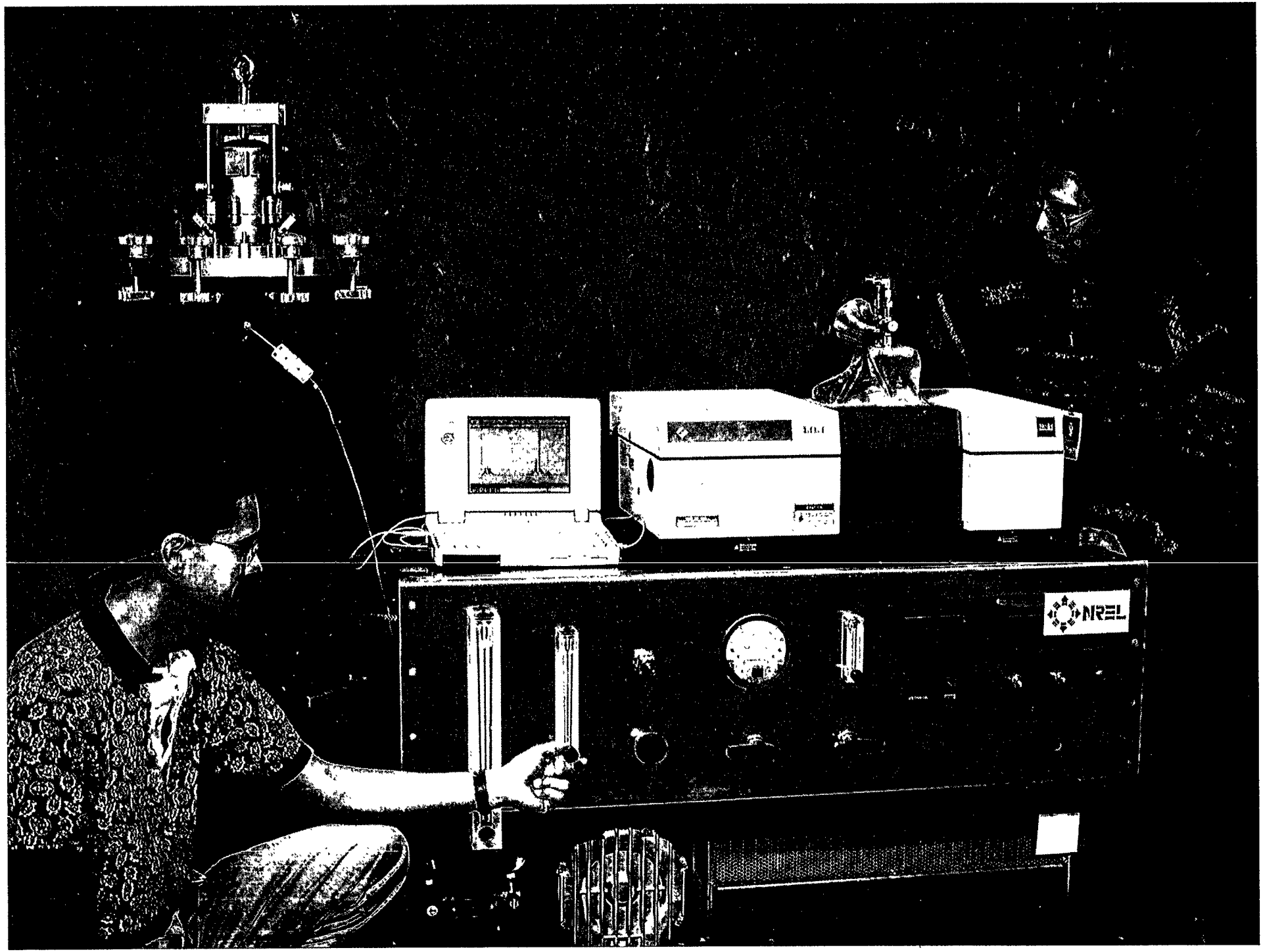


Figure 2. NREL staff member conducting PCO field test at Hewlett Packard, Fort Collins, Colorado.

Figure 3. Photocatalytic oxidation reactor system contained on a cart developed and built by NREL.



Flow Schematic of the PCO Field Test System

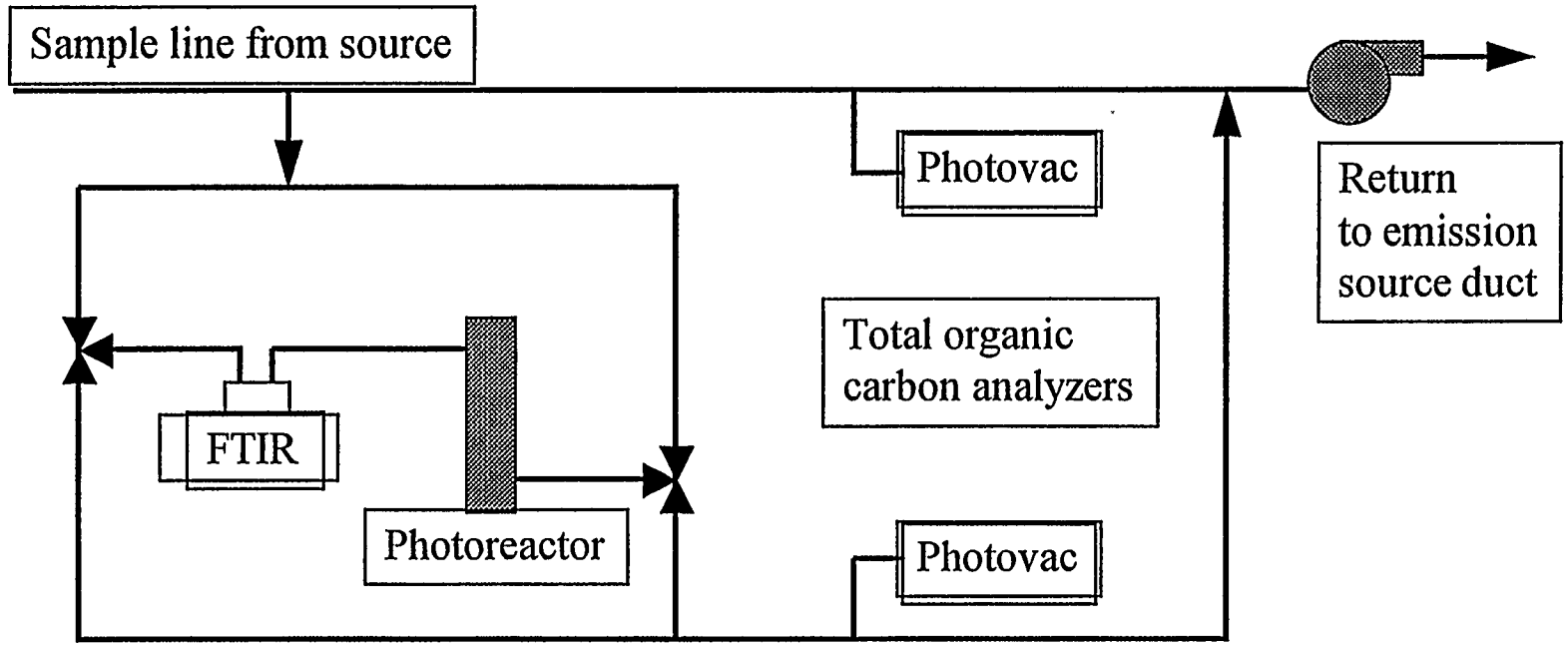


Figure 4

Figure 4. Flow schematic of the PCO field test system used at Hewlett Packard Fort Collins, Colorado, January-February 1996.

oversimplification of a great amount of detailed engineering work but provides a basic view of the HP PCO field test system.

The PCO reactor parameters were flow rate = 2 standard L/min. and temperature = 150°C. The data depicted in Figure 5 is from a cleaning bench and the primary compound is acetone. The maximum concentration recorded at the inlet was over 3,000 ppmv and the maximum recorded at the outlet was 17ppmv. It is obvious from the inlet data that the bench is used intermittently. Compounds treated were obtained from two different air streams; cleaning benches had isopropanol, acetone and Citrisafe, and phototrack air streams contained: ethyl lactate, Novalak resin, ethyl-3-ethoxyproprionate, hydroxybenzophenone, MEK, 1 methoxy-2-propanol acetate, naphthoquinone diazide, naphthoquinon diazide ester deravative. These are real world examples (not the sort of experiments we would typically set up in the laboratory) but representative of the problems in the real world that is our team mission to solve.

Gas phase solar photoreactor development
(Applied)

The Gas phase solar reactor prototype is currently under development. The solar photoreactor would be used for remote (off grid) remediation application, as a subset of a lamp driven PCO application, or in a hybrid configuration. Preliminary outdoor testing was completed last fall. Figure 6 represents a typical experimental test at the NOEL outdoor test facility in October 1995. The data indicates that as the UV light intensity at the reactor increases the outlet TCE concentrations decrease. Current testing is being conducted indoors in a solar simulator. Engineers are working on a prototype of a new solar photoreactor design.

Remediation of organics in aqueous phase
(Demonstration)

The PCO team is sponsoring research by Solarchem Environmental Systems in the area of homogeneous photocatalyst for solar aqueous PCO application. Solarchem is working towards a pilot site demonstration during the summer of 1996 at a petroleum refinery/chemical plant. The Solarchem project includes design, fabrication and demonstration of a pilot scale homogeneous solar PCO system which uses Solaqua, a liquid ferrioxalate catalyst that absorbs 18% of the solar spectrum to efficiently form hydroxyl radical when hydrogen peroxide and light are added. The pilot site demonstration will include testing two or more types of aqueous waste such as a process stream from a polyvinylchloride plant and a stream from oil refinery BTEX contaminated water. The Solarchem PCO process works particularly well with chlorinated unsaturated hydrocarbons, TCE, PCE and BTEX compounds (characteristic of aqueous petroleum refining waste streams). The process requires two pH adjustments; the process runs at a pH of 2.8 and the treated water must be discharged at a nearly neutral pH.

Field Test Data from Jan 4, 1996

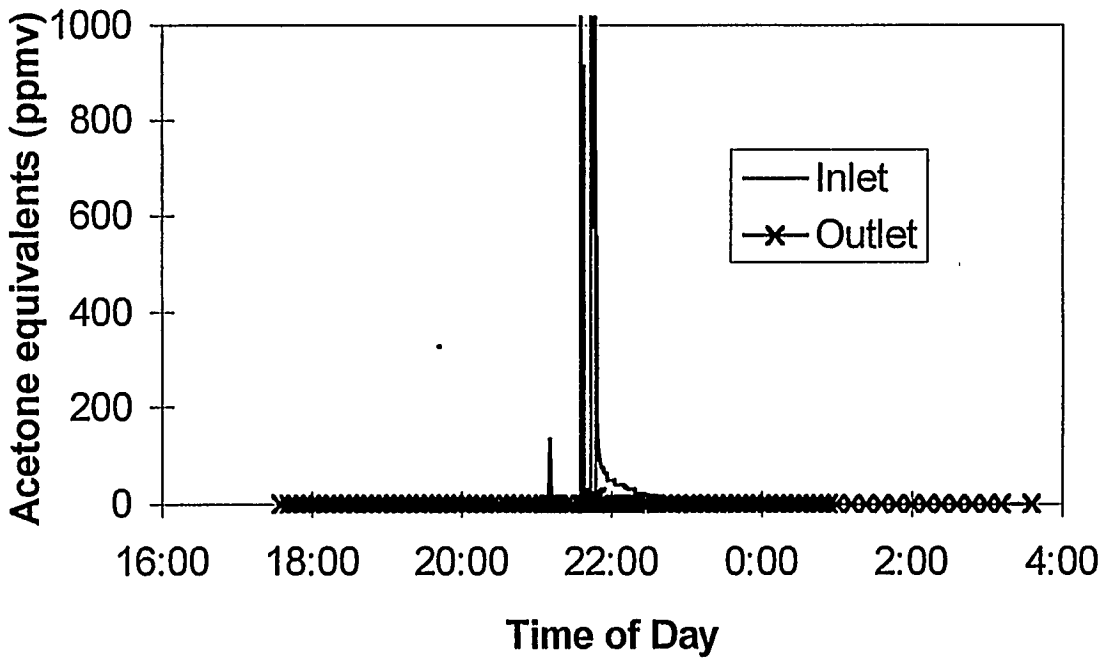


Figure 5. Field test data January 4, 1996 as part of the SEMATECH CRADA.

Figure 5

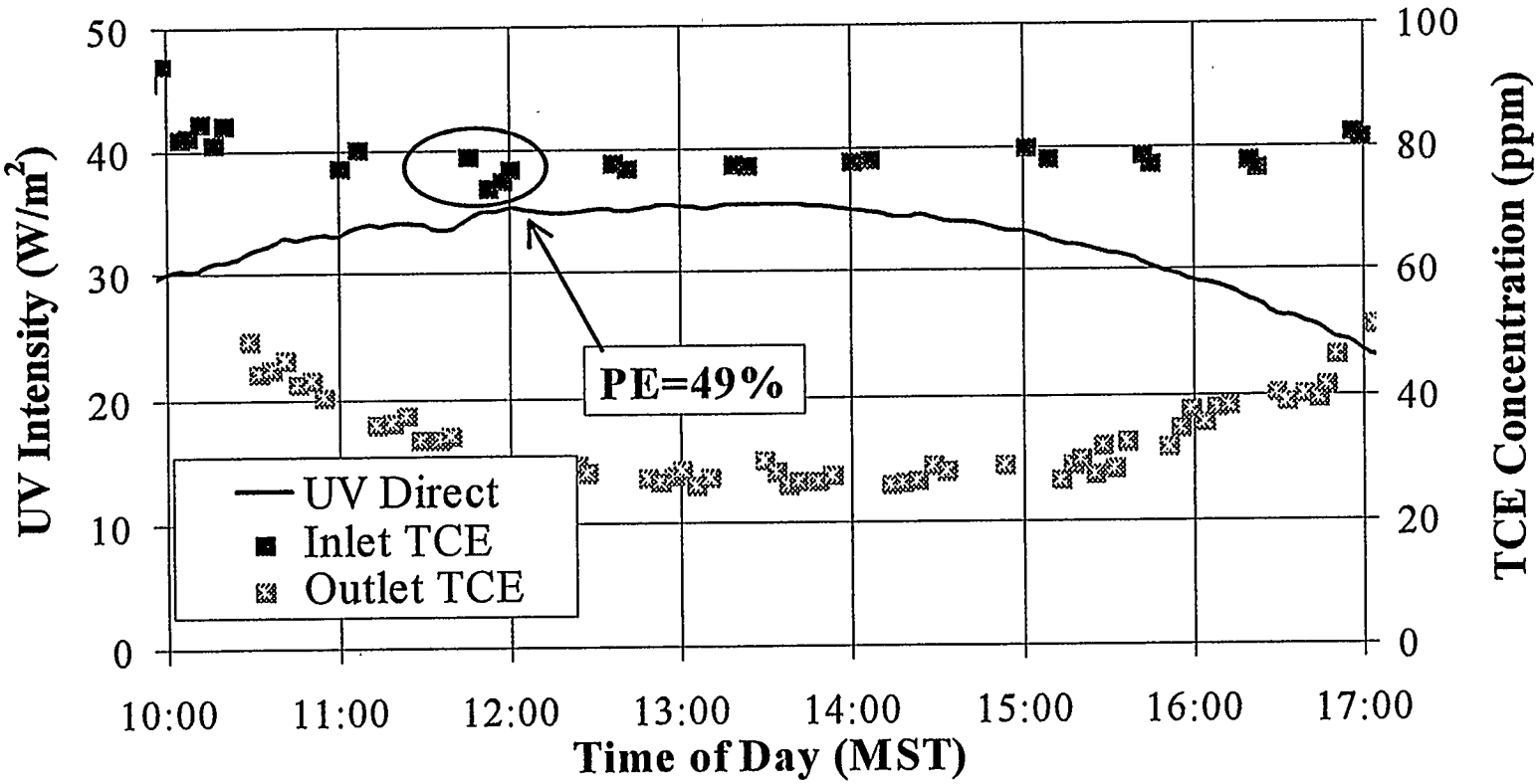


Figure 6. Gas phase solar reactor performance testing data.

Figure 6

New areas of R&D
(Basic)

We are investigating new research in areas such as photoinduced adsorption, high temperature solar PCO, and gas phase PCO for Industries of the Future applications (BTEX applications). Photoinduced adsorption applications include removal of unwanted metal and ion wastes from aqueous or non aqueous streams, concentration of metals or ions in streams and recycling of either metals and ions or solvents. High temperature PCO research includes investigating the combination of heat and ultraviolet light for powering (photo)catalytic waste destruction and determining the feasibility of coupling ultraviolet photocatalysis with thermal catalysis to produce highly efficient waste treatment alternatives. The development of gas phase PCO for Industries of the Future is focused on the Pulp and Paper, Chemical and Petroleum industries.

Application research
(Applied)

Application research includes indoor air quality, hybrid biological/PCO processes for degradative treatment of substituted aromatic pollutants, matrix isolation, remediation of ultra pure water, and drinking water disinfection. Indoor air quality addresses clean room air, ultra-clean micro-environments to house electronic manufacturing operation, bioaerosols (a concern in healthcare facilities and hospital air), and process air/workspace. The hybrid biological/PCO process for degradative treatment of substituted aromatics process should result in the mineralization of a variety of substituted aromatic compounds including hydroxylate-, methylated-, methoxylated-, halognated-, and nitro-aromatics. Initial emphasis is on nitrotoluenes and nitrophenals used in military and industrial processing. Matrix isolation is the study of vibrational, electronic and magnetic resonance spectroscopies of radicals isolated in cryogenic matrices as well as their oxidation chemistry. This information is used in modeling chemical reactions and developing spectroscopic techniques for detection of the radicals. Remediation of ultra pure water applications include water conservation, semiconductor industry use, polishing/remediation for recycle of process water. Catalyst activity improvement is required in order to reach the economic breakpoint for this application. Drinking water disinfection applications for disinfecting water for remote and third world drinking water sites. Research is needed to determine the mechanism of bacterial inactivation by PCO as well as looking at optimized catalysts for disinfection.

Conclusion

The Photochemistry research team conducts research and development work in all R&D areas, basic, applied, demonstration and transfer to commercialization. Basic research includes core PCO R&D and catalysts work as well as conducting research into new photochemistry areas such as photoinduced adsorption and high temperature solar PCO. Applied research work consists of remediation of chloroethylenes in gas phase, gas phase solar photoreactor development, and application research including indoor air quality, hybrid biological/PCO processes and more. We are demonstrating the PCO treatment technology in the gas phase through the SEMATECH CRADA

work and remediation of organics in aqueous phase throyg the Solarchem Environmental Systems. We are working through the IT CRADA to transfer the PCO gas phase remediation technology to IT to commercialize this promising technology. Photochemistry research conducted at NREL does span the R&D spectrum from basic research through technology demonstration with the goal of technology commercialization.

Acknowledgments

We would like to acknowledge the NREL and Sandia PCO team for their research and development work. We would also like to acknowledge our CRADA partners IT, SEMATECH and DuPont and our subcontractor Solarchem Environmental Systems.

NREL BIOFUELS PROGRAM OVERVIEW

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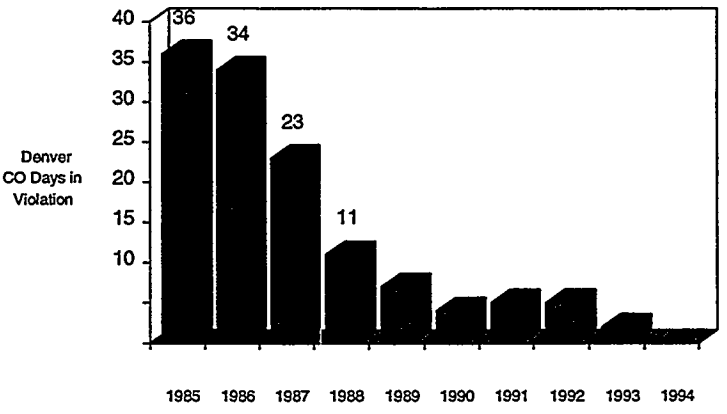
Abstract

The NREL Biofuels Program has been developing technology for conversion of biomass to transportation fuels with support from DOE Office of Transportation Technologies Biofuels System Program. This support has gone to both the National Renewable Energy Laboratory, and over 100 subcontractors in universities and industry. This overview will outline the value of the Biofuels development program to the Nation, the current status of the technology development, and what research areas still need further support and progress for the development of a biofuels industry in the U.S.

Domestic supply of conventional petroleum is the most limited of the country's major energy sources, with a ratio of total estimated recoverable reserves only 16 times the current annual utilization rate (1). To compensate for this, the U.S. is now importing about 55% of its oil supply. Imported oil costs the U.S. about $50 billion annually, is the biggest contributor to the foreign trade deficit, and has a cumulative cost over the last 20 years of $1.3 trillion in current dollars. The EPA has cited estimates that 25,000 to 30,000 jobs are lost for every billion dollars sent abroad for imports, implying that oil imports deprive the U.S. economy of at least a million potential jobs. These current monetary impacts are all the more compelling when it is recalled that the United States transportation sector is totally dependent on petroleum, and that oil prices are presently at their lowest levels in 30 years while both the amount and fraction of oil imported are at their highest levels ever. The nation is thus vulnerable to an interruption of oil supply or an increase in price to an unprecedented extent. Use of biomass-derived alternative fuels such as ethanol, and biodiesel will play a significant role in reducing our nations dependence on foreign oil and the related balance of payments problem.

Use of alternative fuels can also play a significant role in reducing urban air pollution. Specifically, oxygenates added to gasoline help improve the efficiency of combustion, thus improving the oxidation of hydrocarbons to carbon dioxide instead of carbon monoxide (CO), thus decreasing the overall output of CO during operation of motor vehicles. So, use of oxygenates, such as ethanol, is known to reduce carbon monoxide levels emissions from automobile tail-pipes. The use of oxygenates is mandated by the Clean Air Act Amendments of 1990 for 39 locations throughout the U.S. due to the production of unacceptable levels of carbon monoxide in the atmosphere. CO levels are typically higher in the winter months, and therefore, the EPA mandates the inclusion of oxygenate into gasoline during the months of November through February in the non-attainment regions. Atmospheric testing within the City of Denver has supported the value of the use of oxygenates since the CO levels at test locations has been dropping each year during the oxygenate season (Figure 1) from 1986-1994. This has yielded a dramatic decrease in the number of days where the city was in violation of EPA carbon monoxide attainment levels. It is now well recognized among many in the transportation sectors that this decrease in non-attainment days is directly related to the use of oxygenates in the gasoline sold within the Denver region during the winter months.

Figure 1. Denver Carbon Monoxide Trends



Alternative fuels produced from biomass contributes little, if any, net accumulation of carbon dioxide to the atmosphere compared to combustion of fossil fuels, substantially reducing the

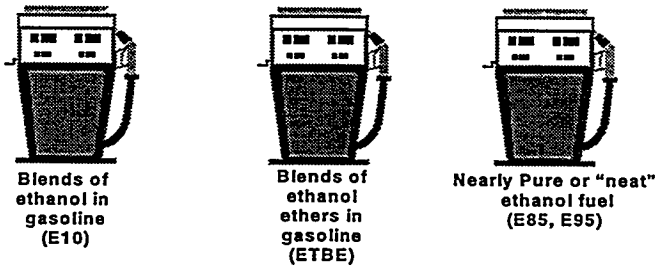
contribution to global climate change by the transportation sector. This occurs because carbon dioxide is recycled in a closed loop between ethanol production and combustion, and the growth of the biomass. Also, small biomass ethanol plants are expected to be powered by the biomass lignin fraction of the feedstock, so limited fossil fuels are required in ethanol production from biomass. For example, it is estimated that 9.3 million metric tons of carbon dioxide emissions will be eliminated for every billion gallons of gasoline displaced by biomass ethanol (2). Conventional transportation fuels, on the other hand, provide no carbon recycle since the carbon source is from fossil carbon that would never be released if the crude oil was not retrieved from the earth.

It is for these reasons that the Department of Energy has been investing significant funds aimed at development of technology for the conversion of biomass materials to ethanol. A significant portion of these funds are going to the National Renewable Energy Laboratory in Golden Colorado to the Biofuels Program which the author manages for DOE and NREL.

The National Renewable Energy Laboratory is unique among the Department of Energy laboratories as it has a single mission of leading the national towards a sustainable energy future by developing renewable energy technologies, improving energy efficiency, and helping to facilitate the commercialization of these technologies. The technologies that NREL is actively pursuing include photovoltaic technology, wind technology, building and energy efficiency systems, waste utilization and conversion technologies, biomass power technologies, and alternative transportation fuel technologies. Within the Biofuels Program, which is funded completely by the Department of Energy Biofuels Systems Program, there are two individual projects. The ethanol project is by far the largest research and development activity, with the biodiesel project being approximately 5% the size of the ethanol project. This manuscript will describe the current activities and directions of the biomass ethanol project at NREL.

The current ethanol industry is comprised of multiple corn-based production facilities located throughout the mid-west. The current U.S. capacity for production of corn-based ethanol is approximately 1.5 billion gallons, with Illinois being the leading producer (3). Ethanol is used as a transportation fuel one of three ways: blending with gasoline as an oxygenate, typically as a 10% blend called E10 is the most common market outlet at present (Figure 2.) (4). A growing use of ethanol is to produce an ether called ethyl tertbutyl ether (ETBE) that serves as an effective oxygenate source that is fully miscible with gasoline. Finally, the use of ethanol as a nearly-neat transportation fuel, typically available at an 85% ethanol/15% gasoline, called E85, is growing within the midwest, particularly among public and private fleets of

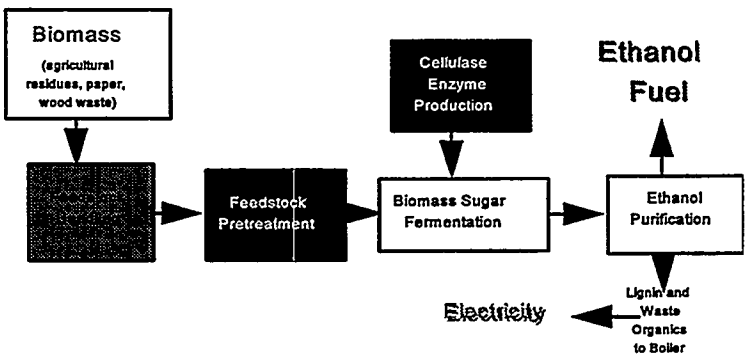
Figure 2. Ethanol Fuel Options



automobiles. Therefore, the future market picture for ethanol use in this country appears to be strong and growing.

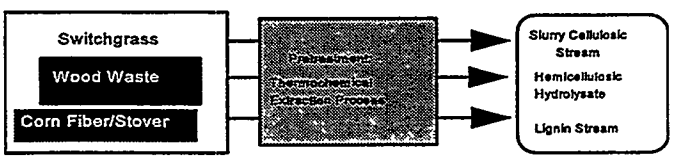
The future for biomass based ethanol is strong as well. Based on the results from an integrated model developed at NREL, it is estimated that about 250 million annual gallons of ethanol will be produced from biomass by the year 2000 if NREL and others continue to receive support from DOE. This support is needed primarily to improve ethanol technology and demonstrate these improvements at NREL with industrial partners that will commercial producers of biomass ethanol. This is the primary mission of the Biofuels Program.

Figure 3. Ethanol from Biomass Process



The technology used to produce ethanol from biomass materials is shown in Figure 3. Once the biomass material is brought into a production facility, it is milled or otherwise reduced in size. Following the feedstock handling process, the feedstock is exposed to various levels of acids, typically sulfuric acid, and high temperature for a short period of time to begin the process of breaking down and separating the various components found within biomass, as in Figure 4. The ideal goal of the pretreatment step is to separate the polymeric cellulose and hemicellulose polymers from the lignin that acts as a structural component in plants. Additionally, the hemicellulose, which is a polymer of xylose sugars, should be depolymerized to individual sugars if the pretreatment conditions are correct. Determining the proper conditions for the pretreatment of biomass materials is not simple since the target biomass can be as diverse as old newspapers, saw dust, corn residues, or prairie grasses. Therefore, pretreatment technology is an area of active research at NREL and with our university and industry subcontractors. Specifically, NREL and our subcontracting partners are working to eliminate sulfuric acid as a pretreatment acid by substitution with organisms or other mild acid that is more environmentally compatible. Additional future research activities will be aimed at softwood forestry residues, green yard waste, rice straw, and grass straw, as well as possibly sugar cane residues. All these different biomass materials are either waste or residues from industry. However, each of these materials will be different enough that specific pretreatment conditions will need to be determined for maximal liberation of the sugar polymers from the lignin.

Figure 4. Feedstock Pretreatment Process



As Figure 3 indicates, the next step in the biomass-to-ethanol process is the processing of the cellulose polymers to glucose sugar. The breakdown of the cellulose polymer occurs due to the action of enzymes called cellulases. In the process at least three

different enzymes are required for complete breakdown of the cellulose sugar polymers. Enzymes called endoglucanases, beta-glucanases, and exoglucanase are all required for efficient breakdown of the cellulose to sugars. This enzymatic attack is shown pictorially in Figure 5 (5) where all three enzymes are active breaking down the cellulose polymer. Unfortunately, the microorganism found in nature do not carry out these degradative processes as rapidly as desired for an industrial process. This is not unexpected because the breakdown of biomass, such as wood chips, is relatively difficult and is a slow process in nature.

As a means of speeding up the process, NREL has had an active program to develop better, cheaper, and faster cellulase enzymes. So, over the last five years, NREL and our subcontractors have undertaken a careful screening of soil samples from throughout the world looking for microorganisms that produce superior cellulase enzymes, and now has a catalogue of cellulase enzymes and a small collection of genetic material that produces these cellulase enzymes. Work with subcontractors as well as in-house staff is under way to develop new combinations of these cellulase enzymes. The overall goal is to develop an ideal mixture of the three different types of enzymes that work synergistically together in a superior manner compared to cellulase mixtures produced by microorganisms found in nature (Figure 5). This biotechnology research has reached the stage of combining new enzymes together to produce sufficient quantities of this new mixture to be tested in the biomass ethanol process. The selected enzymes have been obtained from both fungi and bacteria, their genes have been genetically cloned and produced in the laboratory. Areas of active research that remain for NREL and other research groups include over-production of the enzymes for use in large scale testing, and further improvement of these enzymes functional characteristics by protein engineering. These approaches are underway at NREL and with our subcontractors, but further research is needed to more rapidly improve the ability of this unique mixture of enzymes to convert the biomass cellulose to glucose as quickly and inexpensively as possible.

Figure 5. Cellulases Synergistic Action on Cellulose

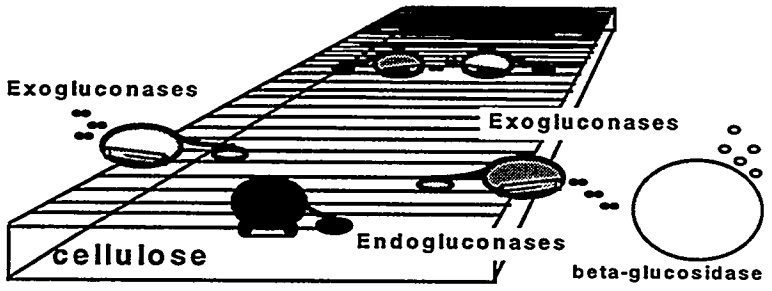
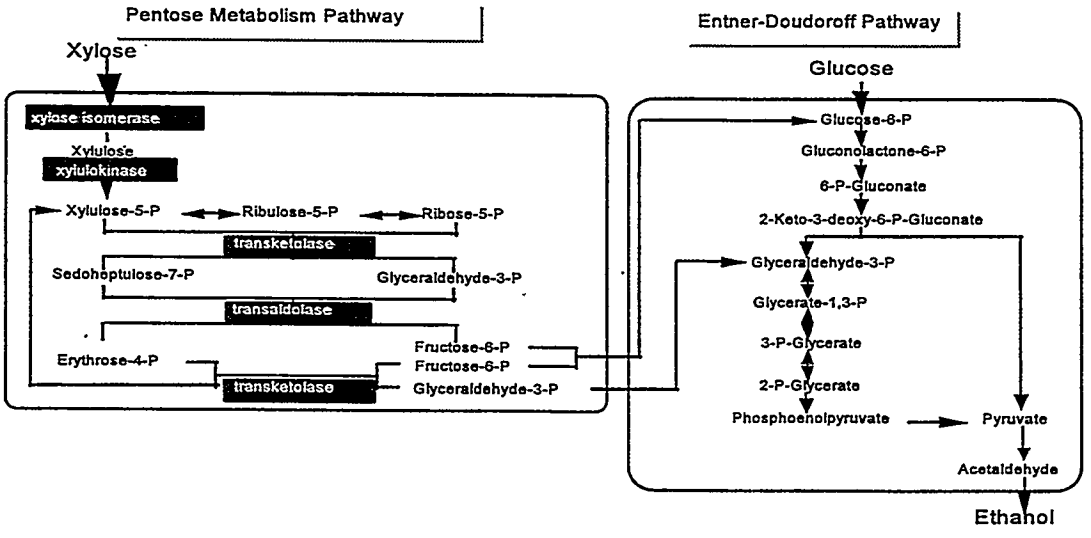


Figure 3 depicts the most efficient fermentation process where simultaneous with the cellulase enzymes attack on the cellulose, a yeast or other microorganism is present in the vessel to immediately absorb the liberated biomass sugars. The resident microorganism, usually a yeast, then rapidly ferments these sugar molecules to produce ethanol. This fermentation process is called simultaneous saccharification and fermentation (SSF). The fermentation of biomass sugars to ethanol is the third area of research supported by active research at NREL and with subcontractors. As outlined earlier, the two types of biomass polymers yield different sugars. Fortunately, both sugars-types from hemicellulose and cellulose can be fermented to ethanol. Unfortunately, the

hemicellulose derived sugars, typified by the five carbon sugar xylose mentioned earlier, is often not fermented by the yeasts that currently produce over one billion gallons of ethanol in the corn-ethanol plants throughout the midwest. Three years ago NREL scientists investigated all possible microorganisms able to produce ethanol as a sole by product. Among the candidates that were identified were a number of yeast, fungi and a bacteria. Upon further analysis, it was determined a well known, safe bacteria that has been used to produce alcoholic beverages in South America for centuries, called *Zymomonas mobilis*, had all the characteristics necessary to be a superior fermentative microorganism compared to yeast except the ability to ferment xylose sugar to ethanol. Since the hemicellulosic sugars, commonly known as the xylose, can comprise up to 25% of the total day mass of the plant material, fermentation of this sugar to ethanol was necessary to obtain optimal economics. Therefore, NREL undertook an advanced genetic engineering program to add the fermentation capability for xylose convention to ethanol to the selected *Zymomonas* bacteria.

This scientific feat has been accomplished by the addition of four different genes that are necessary for the xylose metabolism pathway (6). The genes for these four enzymes were added to *Zymomonas*, and the bacteria then successfully expressed these genes for enzymes for the metabolism of xylose. This permitted the *Zymomonas* bacteria to successfully link the xylose metabolism biochemistry pathway to that of the glucose to ethanol pathway. Therefore, when these genes were added and successfully expressed by the bacteria, a new biochemical pathway was created, as shown in Figure 6 (6), thus permitted the *Zymomonas* to successfully produce ethanol both from glucose and xylose. This development was deemed to be of significant value so it was awarded an R&D 100 award by *R&D* magazine as being one of the most technologically significant new products developed during the year (7). It is anticipated the use of this new "cofermentative" *Zymomonas* strain will permit significantly lower ethanol to be produced from biomass sugars xylose and glucose due to a shorter, much more complete fermentation completed by one type of ethanologenic microorganism.

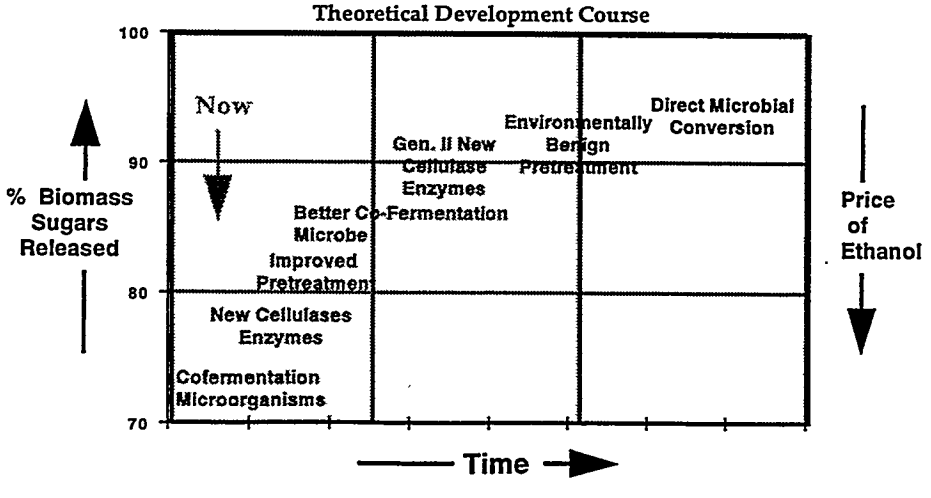
Figure 6 Metabolic Engineering of Zymomonas



This pathway engineering must be thought of as an approach that can be utilized for any changes necessary for a microorganism destined for industrial use. Therefore the opportunities for significant further modifications and improvement is very real and will be the subject of further on-going research within NREL and with our subcontracting partners. In fact, the type of chemical engineering, genetic and biochemical engineering described above for both pretreatment, cellulase, and *Zymomonas* improvements would not have been possible without the basic research efforts of other universities and laboratories. Therefore, there is an on-going need for continuing basic energy research as supported by the Department of Energy and other federal agencies.

The overall drive for technology development within the ethanol produce is to reduce the cost of ethanol being produced from biomass. This will be accomplished by increasing the overall efficiency of conversion of all available sugars from a given type of biomass source. These improvements will likely take place through three improvement areas which have been previously described. Improving the pretreatment process to both release more of the polymeric sugars from the lignin in the biomass, while further decreasing the overall negative environmental impact of pretreatment are two specific goals of the Program. Improvement in the fermentation organism, such that it converts more of the sugars more rapidly, will further improve the process economics. Improved cellulase enzymes necessary for the breakdown for the polymeric glucose in cellulose will also be an area of cost savings. Through the improvements in pretreatment, fermentation and enzyme development, NREL, DOE, and our subcontractors hope to obtain over 90% conversion of the biomass sugars as quickly as possible (Figure 7). The time necessary to carry out these improvements and the exact impact on the price of ethanol is yet to be determined, but it is clear there is a direct relationship between the efficiency of sugar conversion and decreasing cost of the resultant ethanol. These improvements will all require both basic and applied research knowledge that must be continually funded over the next number of years.

Figure 7. Technology Improvements: Key to Reduced Ethanol Cost



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RESEARCH OPPORTUNITIES IN PHOTOCHEMICAL SCIENCES FOR THE DOE HYDROGEN PROGRAM

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Abstract

For several decades, interest in hydrogen has ebbed and flowed. With the OPEC oil embargo of the 1970's and the promise of inexpensive nuclear power, hydrogen research focused on fuel applications. The economics and the realities of nuclear power shifted the emphasis to hydrogen as an energy carrier. Environmental benefits took center stage as scientists and politicians agreed on the potential threat of carbon dioxide emissions to global climate change.

The U.S. Department of Energy (DOE) Office of Utility Technologies manages the National Hydrogen Program. In this role, the DOE provides national leadership and acts as a catalyst through partnerships with industry. These partnerships are needed to assist in the transition of sustainable hydrogen systems from a government-supported research and development phase to commercial successes in the marketplace. The outcome of the Program is expected to be the orderly phase-out of fossil fuels as a result of market-driven technology advances, with a least-cost, environmentally benign energy delivery system.

The program seeks to maintain its balance of high-risk, long-term research in renewable based technologies that address the environmental benefits, with nearer-term, fossil based technologies that address infrastructure and market issues. National laboratories, universities, and industry are encouraged to participate, cooperate, and collaborate in the program. The U.S. Hydrogen Program is poised to overcome the technical and economic challenges that currently limit the impact of hydrogen on our energy picture, through cooperative research, development, and demonstrations.

Introduction

Hydrogen will join electricity in the 21st century as a primary energy carrier in a sustainable energy future. Hydrogen and electricity will ultimately come from renewable energy sources, although fossil fuels will provide a long-term transitional resource. Future hydrogen suppliers will deliver a significant portion of our energy for transportation and other applications. For these applications, hydrogen offers a nonpolluting, inexhaustible, efficient, and potentially cost-effective energy system derived entirely from domestic energy sources. To encourage and support the development of safe, practical, and economically competitive hydrogen technologies and systems, DOE conducts research in the production, storage, and use of hydrogen.

DOE provides national leadership and acts as a catalyst through partnerships with industry. These partnerships are needed to assist in the transition of sustainable hydrogen systems from government-supported research and development to commercial successes in the marketplace. The outcome of the program is expected to be the orderly phase-out of fossil fuels as a result of market-driven technology advances, with a least-cost, environmentally benign energy delivery system. The goals of the program include doubling, by the year 2005, current hydrogen use in the chemical and petroleum sectors as a feedstock for reformulated gasolines. In addition, the program has set a goal for 25% of all new vehicles sold in the United States in 2010 to be hydrogen powered, either as hybrids or as fuel cell vehicles. This will result in an important reduction in NO_x, CO, and CO_2 emissions. A significant portion of the hydrogen required for these vehicles will be produced from biomass and municipal solid waste gasification and pyrolysis. Finally, the program has set a goal of an 8%-10% hydrogen contribution to the total energy market by 2025.

Legislative Actions

Legislative initiatives are in place to facilitate the incorporation of hydrogen into the United States' energy economy. The Hydrogen Research, Development, and Demonstration Program Act of 1990 (often referred to as the Matsunaga Act, after the late Senator Spark M. Matsunaga of Hawaii, who sponsored the legislation), established a number of requirements for the program. DOE prepared a comprehensive 5-year program management plan for hydrogen research and development, with renewable energy as the primary source for the production of hydrogen. An implementation plan for a technology assessment and transfer program among other federal agencies was also developed. The legislation shifted the focus of the program to emphasize production from renewable resources, with fossil fuels serving only in the transition to hydrogen production from renewable resources.

The Matsunaga Act also established the Hydrogen Technical Advisory Panel (HTAP), which advises the Secretary of Energy. The panel is appointed by the Secretary of Energy and consists of representatives from industry, universities, professional societies, government laboratories, financial, environmental, and other appropriate organizations. The panel makes recommendations to the Secretary of Energy on implementing and conducting the program; economic, technical, and environmental consequences of hydrogen production and use; and improvements to the comprehensive 5-year plan.

The Energy Policy Act of 1992 supplemented the Matsunaga Act by requiring the assessment and development of hydrogen production from renewable resources; systems for hydrogen storage that may be suitable for electric vehicles powered by fuel cells; natural gas pipelines to carry hydrogen; and other research and development programs as deemed necessary by DOE.

Recent legislative action includes a bill that will extend and expand the Matsunaga Act. Current bills in the U.S. House of Representatives and the U.S. Senate call for a substantial increase in funding, and industry participation in research, development, and demonstration projects. The Hydrogen Future Act of 1995, which will extend many of the provisions of the Matsunaga Act, was passed by the House of Representatives and awaits action by the Senate.

Program Activities

The Hydrogen Program provides rapid and aggressive implementation of a well-balanced portfolio of research and development projects that minimize technology risks. The development and demonstration of processes and technologies to produce, store, transport, and use hydrogen form the basis of the effort. Through interactions with other federally funded programs, the Hydrogen Program is able to leverage significant federal research funds.

Production Research

Production research is being conducted in three main areas: photolysis, electrolysis, and thermal processes. Photolytic processes include enzymatic production systems and photoelectrochemical systems. Enzymatic research is focused on isolating bacteria and algae with oxygen-tolerant hydrogenases and efficient photosynthetic systems. Engineering issues include designing systems that are easy to operate and control, and reactors that are efficient. Photoelectrochemical development issues include the separation of hydrogen and oxygen, system costs, and materials of construction. Research in electrolytic systems includes the development of solid electrolytes for water electrolysis at higher temperatures than current systems, and the production of hydrogen using an HBr system. Issues include materials of construction and system costs. Thermal research is being conducted in gasification and pyrolysis systems, with biomass and municipal solid waste as the target feedstocks. Research needs include production cost reduction and improved system integration.

Fundamental and basic research projects are focused on developing an understanding of the phenomena that affect the operation and efficiency of photochemical production processes. Projects are generally structured to explore these phenomena over a 4 to 5 year time frame. In the photobiological area, basic research needs include prevention of unwanted mutations and the limitations of using whole organisms. In photoelectrochemistry, corrosion, material compatibility, and gas separation are important fundamental issues. Fundamental understanding of the kinetics, chemistry, configuration, and separation of products at high temperature are important issues in photochemistry.

Storage Research

Hydrogen storage for stationary and mobile applications presents significant challenges. Recent industry cost-shared research efforts have resulted in potential demonstration projects, with integrated storage systems that are efficient and cost effective. Fundamental research continues in more advanced storage systems, including a number of projects using carbon-based systems and glass microspheres. The goal of the program is to develop storage systems that result in an added cost of 50% or less to the cost of delivered hydrogen. Opportunities exist for cost reductions through capacity and efficiency increases and weight reduction, while maintaining and enhancing system safety and reliability.

The fundamental role of concentrated solar energy in the production of carbon-based storage systems is an important area of research. Research is also focused on understanding the adsorption characteristics of carbon based systems, and developing production techniques that lead to high yields of suitable materials.

Utilization Research

The use of hydrogen in internal combustion engines is being studied in a collaborative effort with other offices in DOE. The work is directed toward the development of a mechanical equivalent to the fuel cell. In a partnership among three national laboratories, industries, universities and DOE, the participants are providing fundamental combustion and engine data, information on hydrogen use in internal combustion engines, chemical kinetics calculations of hydrogen and hydrogen/methane combustion, design of hybrid vehicle, and materials for hydrogen storage systems. The selection of a particular engine by the industrial partner will be based on technical merit and the probability of market penetration.

Fundamental research efforts include understanding the propagation of hydrogen detonation/flame front in the internal combustion engine, and controlling air flow and mixing rates to optimize combustion.

Analysis Activities

The Hydrogen Program uses a number of techniques to evaluate and compare hydrogen technologies and integrated systems. Analytical models have been developed to provide comparisons of advanced and conventional hydrogen energy pathways on an equivalent basis. Studies have been conducted to identify infrastructure issues and to determine potential optimum delivery system designs. An analysis was conducted of hydrogen production via small-and large-scale natural gas steam reformers for vehicle refueling stations. The study focused on the use of zero emission vehicles in southern California, where legislation will likely result in the first use of hydrogen as a motor vehicle fuel. In the study, the large-scale system was centrally located, with hydrogen delivered to refueling stations as compressed or liquid hydrogen. The small-scale system was located at the refueling station, and produced fuel-cell quality hydrogen. Preliminary cost estimates were performed for a

non-optimized design. The reformer capital cost was an important factor in the overall cost of hydrogen.

Economic analysis is also used to identify areas requiring further research and to track research progress. Different levels of analysis are used for fundamental, advanced, and near-commercial processes. The appropriate level depends on the availability of data and system design. Studies are under way to develop base-line economics for current hydrogen production and storage research projects.

Realizing the Hydrogen Future

Our team of researchers is a highly motivated, talented group of scientists and engineers dedicated to seeing hydrogen become an important contribution to the United States' energy future. DOE endeavors to provide technology exchange with industry to facilitate the transition to renewable energy. Increased funding, provided by progressive legislation, will help accelerate the fulfillment of the hydrogen future.

Panel Reports

PANEL A-1

PHOTO ELECTROCHEMICAL AND ORGANIC-BASED SOLAR CELLS

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Abstract

Research in solar photoconversion has resulted in significant advances in the fields of photoelectrochemistry and dye-sensitized solar cells. Progress is also evident in the understanding of solid state organic systems for energy transduction. It is evident, however, that the examination in this report of the accomplishments in these areas serves to highlight the great extent of research that is necessary to establish a technology base sufficient for practical application. Recommendations are made in this report on the directions that this research should take.

PHOTO ELECTROCHEMICAL Solar Cells

Although photosynthesis is the primary energy source for life on earth, only ≈ 3% of the light energy striking a plant is actually stored as chemical fuel. Of course, plants had certain constraints on their raw materials and growth environment, and were therefore not optimized by nature to function solely as energy conversion machines. Photovoltaic cells produce electricity much more efficiently from sunlight than does plant photosynthesis, and such systems have demonstrated field efficiencies in excess of 20%. In fact, the theoretical maximum efficiency for a simple light-absorbing solar energy conversion device is approximately 34%, and this limit has almost been reached in isolated, laboratory photovoltaic cells. However, to achieve such high solar energy conversion efficiencies, very expensive materials, processing, and packaging costs must be incurred. Alternate approaches that might offer comparable efficiencies, for a reduced cost, include PHOTO ELECTROCHEMICAL and organic-based solar cells. Numerous laboratories around the world are therefore pursuing these types of alternatives with the hope of developing systems that will better optimize the cost/efficiency ratio of electricity or chemical fuel production from solar energy as the sole input source in a renewable, terrestrial energy conversion installation.

Semiconductor-based PHOTO ELECTROCHEMICAL cells combine the essential functions of naturally occurring, molecule-based energy conversion systems used in plants with those of the more technologically advanced, semiconductor-based, photovoltaic cells that are used to supply power to spacecraft. PHOTO ELECTROCHEMICAL systems use sunlight to supply part, or all, of the energy required to generate the storable chemical fuels (Figure 1). PHOTO ELECTROCHEMICAL systems also can be utilized to provide electrical energy, if desired. PHOTO ELECTROCHEMICAL energy conversion systems, although a relatively new technology (having only been investigated on a wide scale since 1972), have demonstrated laboratory solar energy conversion efficiencies of >16% for electricity formation or of >10% for fuel formation during the sunlight-assisted splitting of water into $H_2(g)$ and $O_2(g)$. In this respect, they represent a promising method for obtaining renewable, storable energy from the sun, with efficiencies that are too high to ignore as a potentially viable option for obtaining widespread renewable energy from such systems. In addition, PHOTO ELECTROCHEMICAL cells have been demonstrated to retain most of their efficiencies when much less expensive polycrystalline, or even nanocrystalline, semiconductors are used, in contrast to photovoltaic devices whose efficiencies decline severely when such materials are employed.

For perspective on the magnitude of a 15% energy conversion efficiency, an interesting calculation is to compare the energy obtainable from a farm of 15% efficient PHOTO ELECTROCHEMICAL or photovoltaic cells compared to that produced by a nuclear power plant. We will not describe a detailed economic analysis of PHOTO ELECTROCHEMICAL, photovoltaic, or similar systems relative to each other or relative to other available energy sources, however, it is useful to obtain some perspective on the order of magnitude that is being contemplated in any real world application of this technology. In performing such a calculation, we will base the land usage on the area of the nuclear plant and on the surrounding areas dedicated to the installation for safety purposes, which generally might be 2 km by 4 km. A typical nuclear power plant might produce 0.5 GW, or

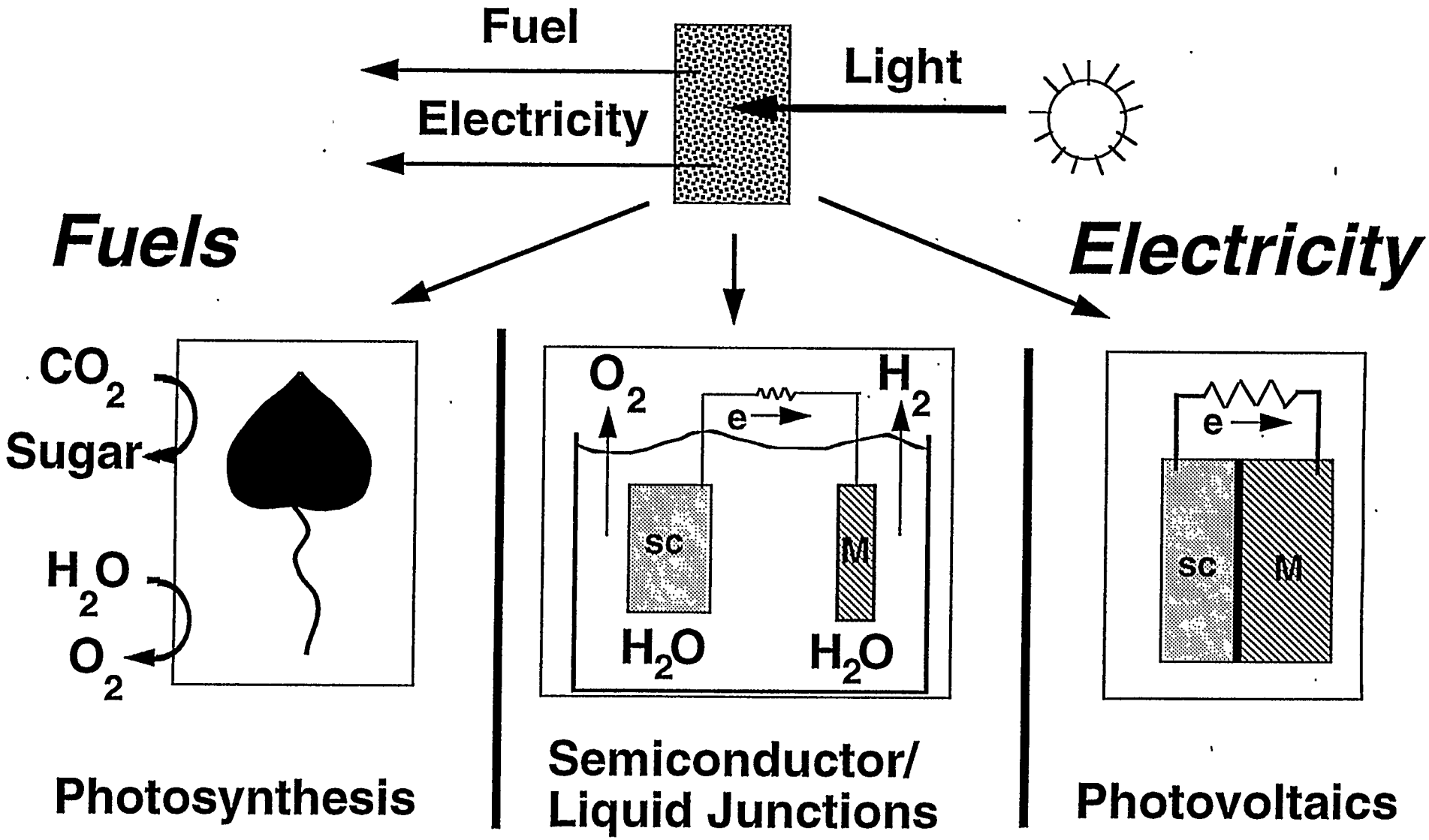


Figure 1. Known Methods for Transforming Solar Energy into Chemical Fuels or Electrical Energy. Photosynthesis stores approximately 3% of the incident solar energy in the form of chemical fuels for use by the plant. Photovoltaics produce electrical energy with up to 25% efficiency. "Wet" solar cells based on semiconductor/liquid junctions produce either storable chemical fuels or electrical energy, depending on their mode of operation. Efficiencies of these artificial photosynthetic systems can be greater than 15%.

$5x10^8$ W. Sunlight at noon of $1x10^3$ W/m^2 striking this same $8x10^6$ m^2 area, at 15% conversion efficiency, produces $1x10^9$ W from the photovoltaic or PHOTO ELECTROCHEMICAL devices covering this same area. Averaging the insolation over an entire 24 hour period produces approximately a factor of 4 loss in average insolation relative to the peak value at noon, yielding roughly $2x10^8$ W on average, i.e., a value within a factor of two of that produced by the nuclear plant (but without operating safety concerns or waste disposal issues). This calculation also assumes that the only source for a photovoltaic or PHOTO ELECTROCHEMICAL energy farm is at a central site, as opposed to augmenting such a site, or even distributing the generation sources, for more local energy generation in a fashion that is not possible with wind, nuclear, and other many other types of energy conversion installations.

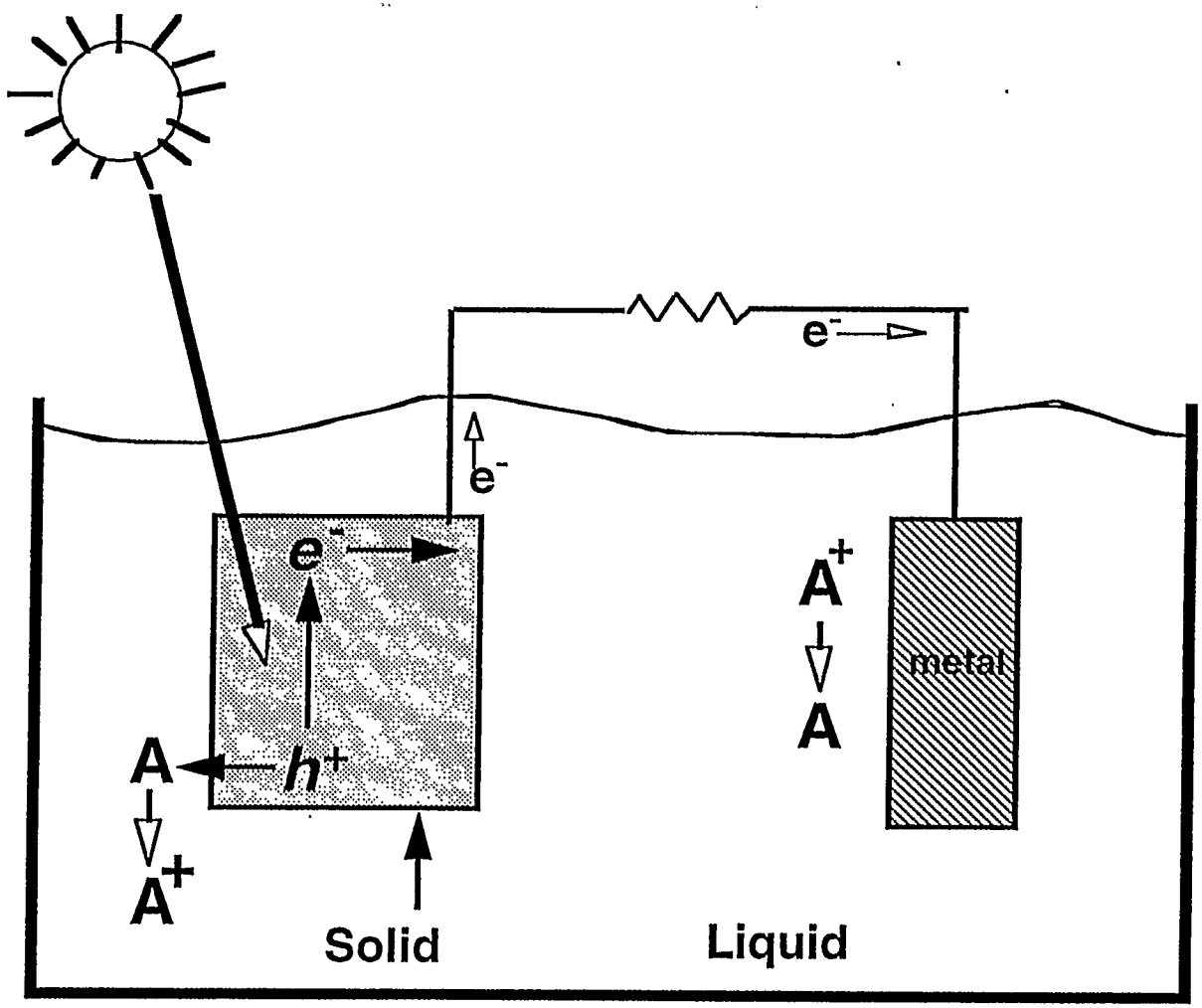
Basic Processes of a PHOTO ELECTROCHEMICAL Energy Conversion Device

A PHOTO ELECTROCHEMICAL cell is closely related to a battery, fuel cell, or other type of electrochemical system, in that it is composed of two electrodes and an electrolyte. Unlike batteries or fuel cells, in which the energy is initially stored in the reactants and is then released through the electrical discharge circuit during the formation of chemical reaction products, PHOTO ELECTROCHEMICAL cells utilize the input optical energy to drive electrochemical reactions (Figure 1). To construct a PHOTO ELECTROCHEMICAL cell, one of the metal electrodes of a conventional electrochemical cell is replaced by a semiconductor electrode. Light absorbed by the semiconductor electrode produces a current through the cell, which results in the production of chemical fuels and/or electrical energy by the device.

The basic processes that must occur in such a system to achieve efficient solar energy conversion are now well-understood scientifically. The semiconductor electrode must have a band gap so that it efficiently absorbs light from the solar spectrum; thus, band gaps of between 1.1 and 1.7 eV (1100 to 700 nm) are desirable for optimal terrestrial energy conversion purposes. Absorption of light by the semiconducting solid produces an excited electronic state. In this excited state, the electron and the electron vacancy (the "hole") are both more energetic than they were in their respective ground states. The photoexcited electrons and holes are generally not tightly bound to an individual atom or set of atoms in the solid. These delocalized charge carriers readily move through the semiconductor, and are therefore available to perform chemical reactions at the solid/liquid interface (Figure 2). When the photogenerated electrons and holes drive chemical reactions at the electrodes in the cell, energy from sunlight is stored in the system.

If the chemical reaction at one electrode is exactly the opposite of the reaction at the other electrode, no net chemical change will occur in the electrolyte. The overall process is then conversion of light into electricity. This mode of PHOTO ELECTROCHEMICAL cell operation resembles that of a photovoltaic device, and is designated as a regenerative PHOTO ELECTROCHEMICAL cell. Alternatively, if the chemical reactions are different at each electrode, chemical fuels will be produced by the light-induced current flow. This type of system is designated as a fuel-forming PHOTO ELECTROCHEMICAL cell. Both regenerative and fuel-forming PHOTO ELECTROCHEMICAL cells have been demonstrated in the laboratory. A particularly appealing

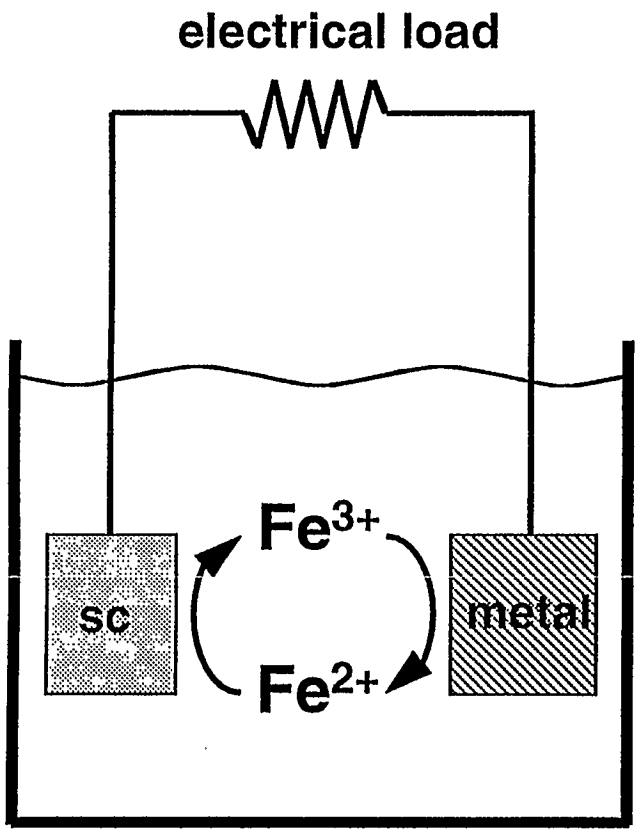
Photoelectrochemical Cell



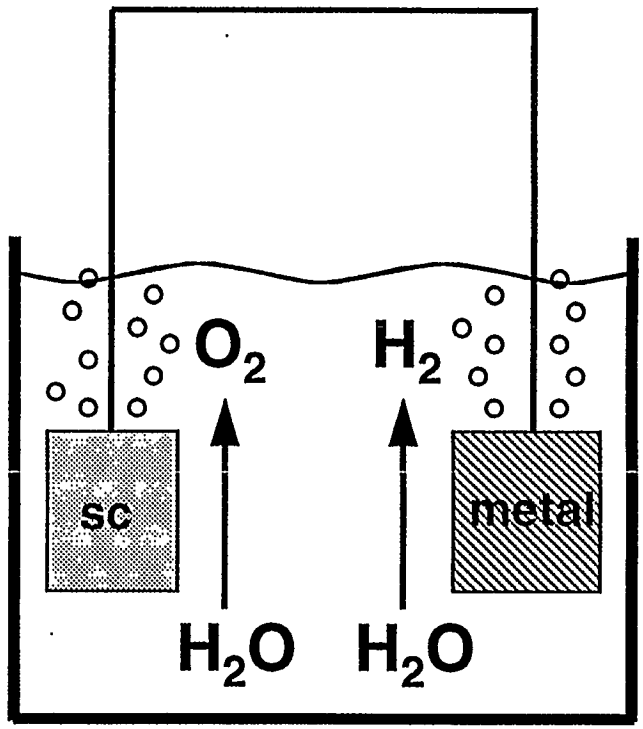
Light is Converted to Electrical and Chemical Energy

Figure 2. Basic Operation of a Photoelectrochemical Cell. The semiconducting electrode absorbs energy from sunlight and produces a current through the electrochemical cell. The current produces electrical and/or chemical energy in the system.

Regenerative vs. Fuel-Forming Cells



No net chemical change



Energy is converted to fuel

Figure 3. Two Modes of Operation for "Wet" Solar Cells Based on Photoactive Semiconductor Materials. In both possibilities shown, the semiconductor (indicated in gray) absorbs the light and produces energetic electrons that can flow through the circuit. The differences between the cells result from the types of chemical reactions that occur in the liquid as a result of this electron flow. a) A "wet" solar cell that produces electrical power from incident sunlight. The semiconductor produces excited electrons which flow through the circuit, doing work on an electrical load. This load could be a light bulb, fuel cell battery, or other type of electrical machinery. The electrons are then injected into the solution at the metal electrode (indicated in blue), and produce a chemical reaction in the liquid. In this example, the injected electrons convert one form of iron (Fe^{3+}, with three ionized electrons) to another (Fe^{2+}, with only two ionized electrons). The Fe^{2+} then moves to the semiconductor electrode, carrying with it the injected electron. To complete the circuit, the Fe^{2+} then donates this electron to the semiconductor electrode. This regenerates the Fe^{3+} state in the solution. Thus, no net chemical change occurs in the liquid, but the light has produced a current through the electrical device in the circuit. b) A "wet" solar cell that produces both electrical power and chemical fuels from incident sunlight. The processes of light harvesting and current flow through the circuit are very similar to case a), but the chemical reactions now are different at the two electrodes. In this example, the injected electrons react with the water to produce gaseous hydrogen (H_2), which bubbles out of the solution. To complete the electrical circuit, the semiconductor electrode must be provided with electrons. In this example, they come from the water itself. Removal of electrons from the water produces oxygen gas (O_2), which also bubbles out of the solution. Thus, illumination of this cell with light produces both current flow and gaseous chemical fuels. The gases could be collected and stored for later use, with the stored energy being recovered either in a fuel cell or by burning the hydrogen and oxygen in an engine to regenerate the water.

situation, which has not been yet realized in efficient, stable PHOTO ELECTROCHEMICAL cells, is depicted in Figure 3, in which water is the liquid and current flow through the circuit simultaneously produces electricity, hydrogen gas, and oxygen gas. Closer consideration of a PHOTO ELECTROCHEMICAL cell makes it clear that efficient light absorption alone is not sufficient to obtain efficient device operation. If the charged carriers created by optical excitation of the semiconductor had no preference regarding their direction of motion, equal numbers of excited electrons would travel in clockwise and counterclockwise directions through the circuit in the cell. The equal magnitudes, but opposite signs, of the currents would lead to a net cancellation of current in the wire, and no net energy output would be obtained from such a cell.

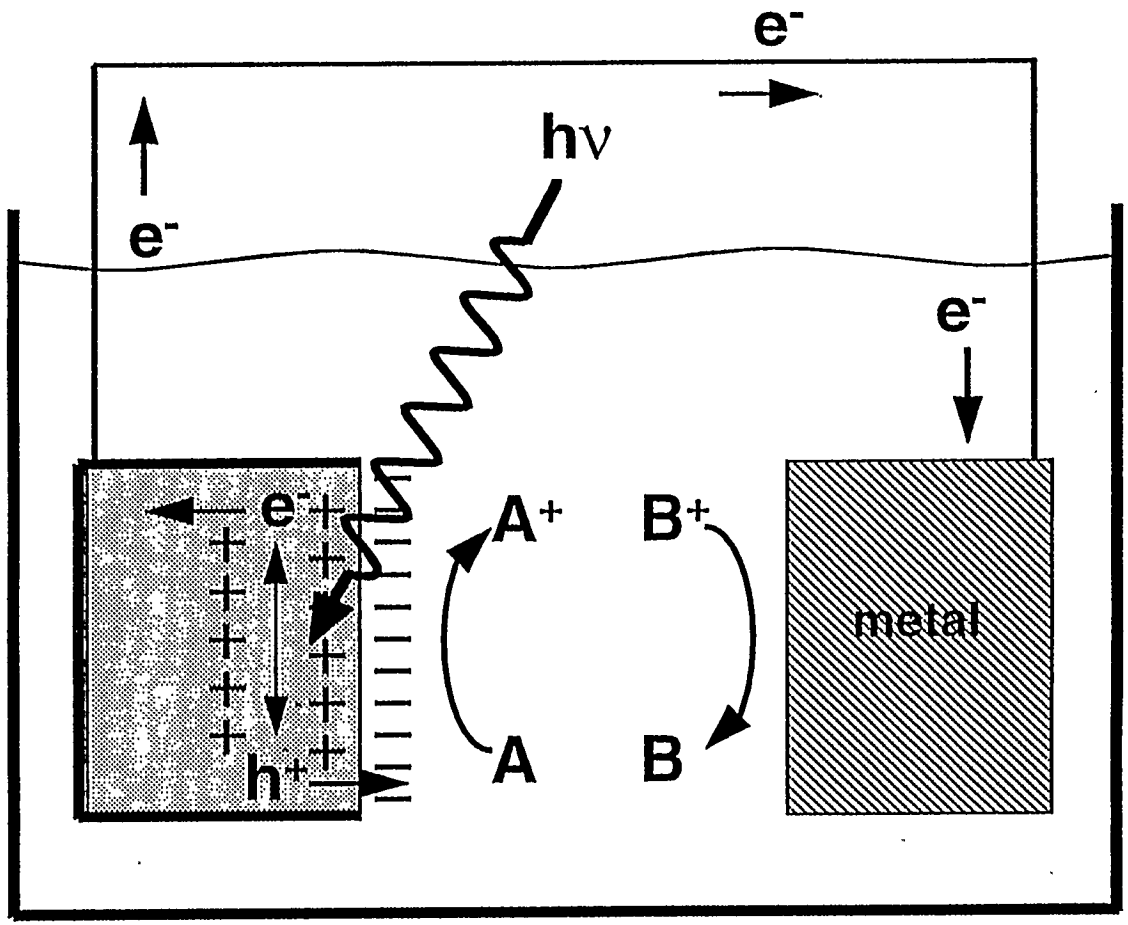
Charge separation is, however, very efficiently achieved in a well-designed PHOTO ELECTROCHEMICAL cell. The key to directing the charge carriers preferentially through the circuit lies in the formation of a strong electric field at the semiconductor/liquid interface (Figure 4). This electric field either attracts or repels electrons from the interface, depending on the polarity of the field. Fortunately, maintaining the field does not require a constant energy input from an external source: this electric field occurs naturally, and spontaneously, whenever two phases with different chemical properties are brought into contact. A typical chemical potential difference between two phases is on the order of 1 eV, and semiconductor samples typically support electric fields for distances of 10^{-5}-10^{-6} cm from their surfaces. This leads to electric field strengths of 10^{5}-10^{6} V-cm^{-1} at the solid/liquid contact. In semiconductor/liquid junctions, the interfacial fields are generally so strong that any photogenerated electrons are rapidly driven away from their point of absorption, and charge recombination is thereby suppressed. Due to the presence of this strong interfacial electric field, the yield of electrons directed through the circuit can be in excess of 90% of the number of photons incident onto the cell, and very efficient energy conversion devices can be obtained.

A promising variation on the basic construction of a PHOTO ELECTROCHEMICAL cell involves using a dye-coated wide band gap semiconducting electrode. The dye is used to harvest the photons of interest in the solar spectrum, while the semiconductor/liquid interface provides the basis for the charge separation that is critical to the operation of an efficient PHOTO ELECTROCHEMICAL cell. The photoelectrode has an extremely high surface area to facilitate efficient light absorption by a single layer of dye molecules that has been deliberately bonded to the electrode surface. This combination allows, in certain instances, use of inexpensive, stable, particulate semiconducting materials to efficiently absorb and convert sunlight into electrical and chemical fuels and has become a highly visible, extremely active area of PHOTO ELECTROCHEMICAL cell research in the past few years.

Major Issues in Development of Efficient PHOTO ELECTROCHEMICAL Energy Conversion Systems:

Although PHOTO ELECTROCHEMICAL cells are simple to fabricate and straightforward in concept, they present a number of scientific and engineering challenges in conjunction with their potential implementation as widely adopted, fieldable energy conversion devices. These challenges include:

Semiconductor/Liquid Junction Electric Field



Interfacial electric field separates photogenerated charge carriers

Figure 4. Schematic of a "Wet" Semiconductor/liquid Based Solar Cell. The light is absorbed by the semiconductor and produces excited electrons. The semiconducting material could be silicon, gallium arsenide, titanium dioxide, or other suitable samples. The excited electrons are directed into the wire by the electric field (indicated by the black and white charges), because the negatively charged electrons are repelled by the negative charges that reside on the liquid side of the semiconductor/liquid boundary. The electrons then flow clockwise through the circuit, performing work through a load. They then reach the metal electrode and are forced to undergo a chemical reaction with the liquid in order to continue the circuit. The chemical produced from this reaction then moves through the liquid, and reacts with the semiconductor electrode. This restores the electron to its original position and completes the current loop.

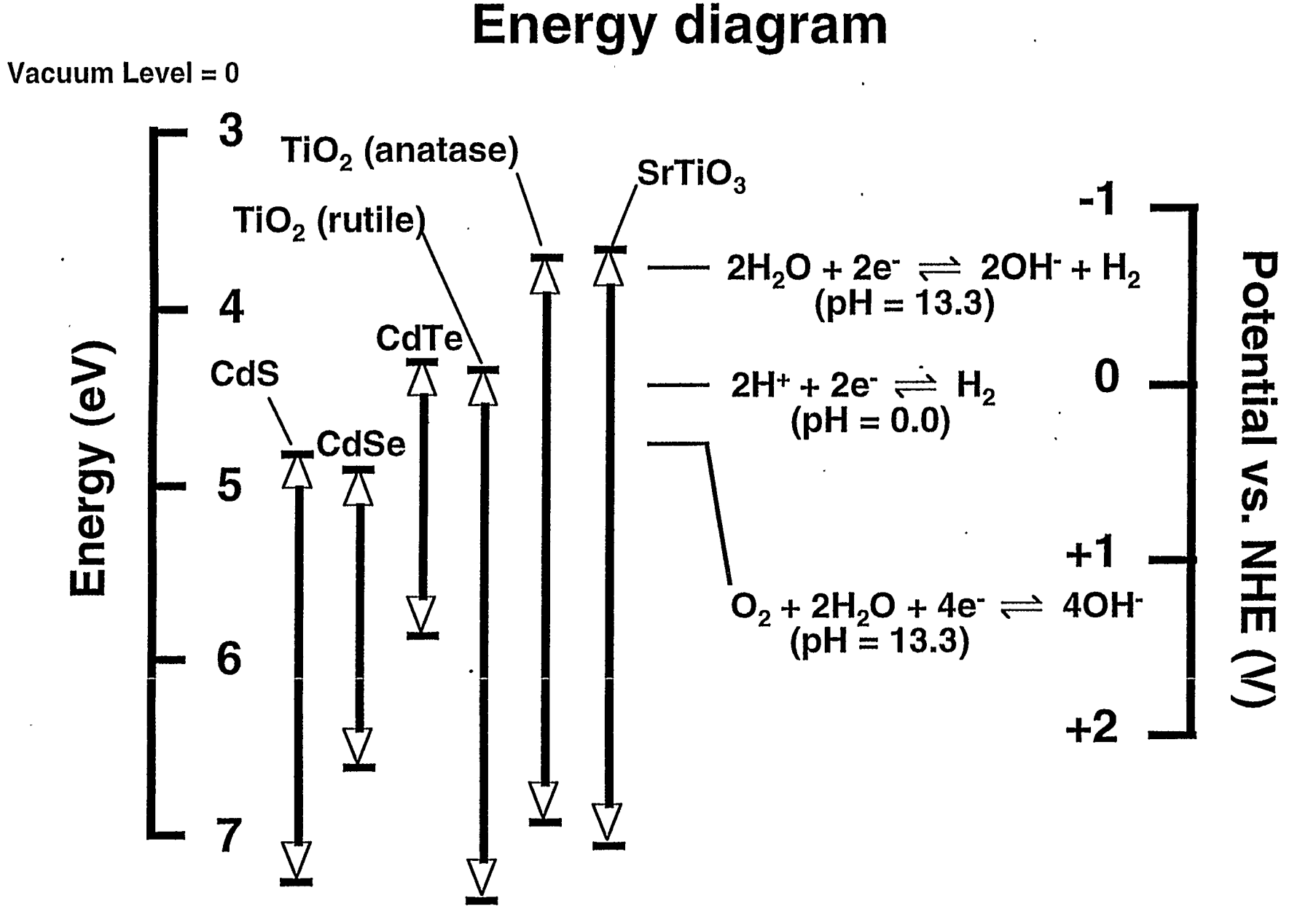


Figure 5. Energy Levels of Various Solids and Liquids used in Semiconductor/liquid Junctions for Artificial Photosynthesis. Efficient energy conversion requires that little energy is wasted when charges are transferred from the absorbing solid into the liquid phase. Metal oxide semiconductors, like TiO_2, have energy levels that are close to the energy levels of water reduction, but are not well matched to the oxidation of water to O_2. Such absorbers therefore waste significant energy in the electrolysis of water. Non-oxide materials have smaller band gaps and waste less energy, but are unstable to corrosion or passivation in sunlight.

- improving the stability of PHOTO ELECTROCHEMICAL cells, especially those operating in aqueous electrolytes;

- improving the efficiency of desirable photoelectrode/electrolyte combinations through chemical control over the bulk and surface properties of the solid and control over the composition of the electrolyte;

- discovering new semiconducting materials or surfaces with desirable properties, such as significantly reduced manufacturing costs, increased efficiency in water photoelectrolysis applications and improved stability in certain desirable electrolytes.

- discovering new catalysts to enable the energy-efficient multi-electron transfer reactions necessary for PHOTO ELECTROCHEMICAL fuel formation.

These major issues form the basis for many of the near and mid-term research programs in this field in the future, and are described in more detail in the remainder of this report.

Stability of PHOTO ELECTROCHEMICAL Cells in Aqueous Electrolytes

Although the modern field of photoelectrochemistry was revived in 1972 with the discovery that TiO_2 could be used to electrolyze water, forming hydrogen and oxygen gases from sunlight (Figure 1), little progress in identifying materials that are suitable for the efficient, stable, unassisted photoelectrolysis of water has been made since that date. A variety of metal oxides have been investigated, and those that provide stable photoelectrodes in aqueous solution have low solar efficiencies, due to their wide band gaps and resulting unfavorable overlap in absorption with photons present in the terrestrial solar spectrum. In addition, the lattice anion is thought to control the energetic position of the valence band of the semiconductor. Thus, for all the metal oxides evaluated to date, the valence band is far too positive relative to what is required thermodynamically to evolve oxygen from water, and decreases in the band gap of metal oxides merely prevent formation of hydrogen gas while not improving the thermodynamics or kinetics of the oxygen evolution process (Figure 5). Non-oxide semiconducting materials with potentially higher efficiencies either rapidly passivate or corrode in aqueous solutions. Thus, efficiencies of unassisted water photoelectrolysis remain in the range of 1-2%.

There is no reason, in principle, why these limitations cannot be overcome. *New materials are required in order to obtain photoelectrodes having the right band gap and stability properties in aqueous solution.* Since there are at present very few accepted fundamental principles to guide this search, little research efforts are ongoing in this area of photoelectrochemistry. However, there is a great opportunity for achieving a significant advance in PHOTO ELECTROCHEMICAL energy conversion if such materials could be identified. Perhaps new oxides of different chemical structures, related to research in superconductivity, or other new semiconducting solids, such as oxysulfides, would prove suitable for this important purpose.

Optimum Absorption Threshold

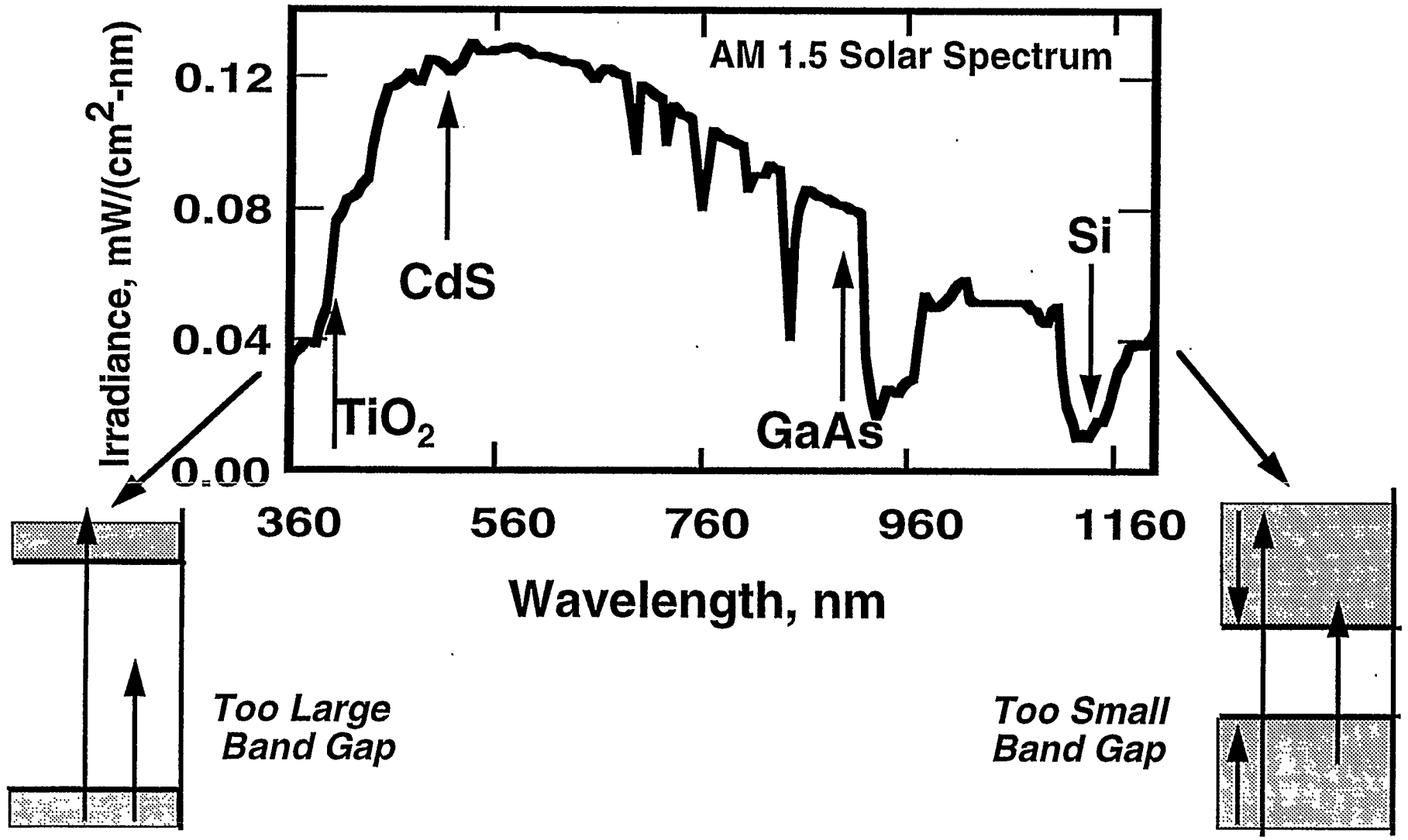


Figure 6. Spectral Properties of Sunlight Striking the Earth's Surface. Absorbers of sunlight must be optimized in order to most effectively convert solar energy into electrical and/or chemical energy. The band gap of a material is the energy below which no light is absorbed, and above which it absorbs light effectively. Materials with very large band gaps, such as CDs or TiO_2, are not effective for artificial photosynthesis because they do not absorb a significant portion of the solar spectrum. Materials with very small band gaps, such as Ge, absorb a large fraction of the solar energy; however, the excess energy of most carriers in Ge is converted to heat, leaving only a small fraction of the photon energy to be converted to useful fuels or electricity. The optimal conversion efficiency is achieved for absorbers having band gaps between 1100 and 900 nm, such as Si, GaAs, and InP.

A related scientific issue involves understanding the kinetics and mechanisms through which otherwise desirable semiconductor materials corrode in aqueous solution. The common semiconductors used in computer circuits and photovoltaic cells, such as silicon (Si) and gallium arsenide (GaAs), would be near-optimal for use in PHOTO ELECTROCHEMICAL cells, because their absorption spectra are nearly ideally matched to the solar spectrum for efficient harvesting of optical energy (Figure 6). However, these semiconductor materials do not allow simple construction of a energy storage system by immersion of the solid into water. Upon exposure to light, Si photoelectrodes form an insulating layer of SiO_2 (sand) which stops current flow, and GaAs photoelectrodes dissolve away where illuminated, destroying the electrode material.

One approach to circumventing this problem is to search for water-soluble molecules that exchange electrons with the photoelectrode much more readily than does water. Such molecules, if present in the liquid in sufficient concentration, could prevent electrode corrosion by reacting with the photogenerated holes in the electrode before the holes can participate in the corrosion process. If the oxidized form of these corrosion-inhibiting reagents also happens to provide a useful fuel, the system becomes even more desirable.

This approach has been successfully implemented for stabilizing cadmium sulfide (CDs) electrodes in aqueous sulfide solutions and to GaAs electrodes in aqueous selenide solutions, as well as for a number of other semiconductor/liquid interfaces. In favorable cases, long term stability for several years has been demonstrated through use of this approach, and solar energy conversion efficiencies as high as 16% have been observed using this approach (Figure 7). The use of the stabilizing agent eliminates the possibility of production of desirable chemical fuels from the PHOTO ELECTROCHEMICAL process, but in return provides a stable PHOTO ELECTROCHEMICAL cell for the conversion of light into electrical power.

Although this strategy works very well in certain cases, there are currently no principles to guide identification of which electrode/electrolyte combinations will provide stable PHOTO ELECTROCHEMICAL cells. To illustrate the degree of stability that is required for long-term cell operation, if >99.9% of the charge carriers were to react with the stabilizer and only 0.1% were to react in a corrosion reaction, a 1 μm thick GaAs photoanode would only operate for ≈5 days in sunlight before it would corrode entirely. Thus, in the presence of the solvent (water) as an undesired competitor for these charge carriers, greater than 99.99% of the reaction products must be directed towards the stabilizing agent to obtain a stable cell for 10 years of operation. For some materials, such as CDs, several stabilizer-electrolyte combinations have been identified that are stable on the months/years time scale, while for others, such as Si photoanodes, no reagent has been discovered that provides stable operation even on the time scale of minutes in aqueous solution. *Research into the underlying, fundamental mechanisms by which semiconductor electrodes corrode or passivate in aqueous solutions, and into mechanisms for competing successfully with these undesirable reactions, also could potentially have great impact in advancing PHOTO ELECTROCHEMICAL energy conversion.*

n-GaAs/liquid Photoelectrochemical Cell

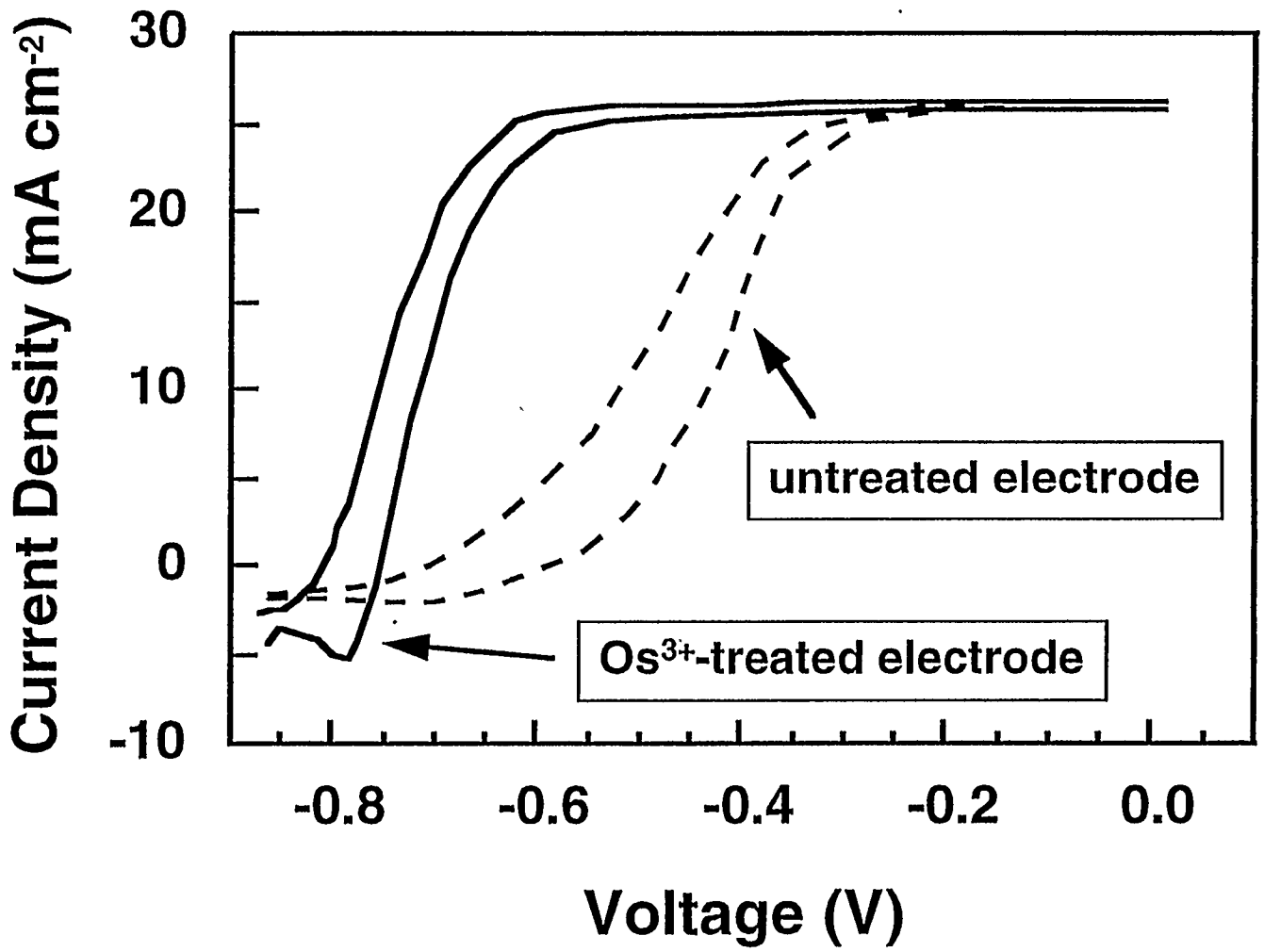


Figure 7. Current-Voltage Behavior of Photoelectrochemical Cells. Current-voltage behavior of GaAs/liquid junction photoelectrochemical cells. The untreated, etched GaAs surface yields 8-9% energy conversion, while chemisorption of Os^{3+} or other catalysts improved the energy conversion efficiency at maximum power to 15-16%.

Understanding Interfacial Charge Transfer Kinetics as a Basis for Obtaining Improved Photoelectrode Stability and Efficiency

A related area in need of fundamental understanding is the rate of charge transfer from a delocalized charge carrier (either a photogenerated electron or hole) in the semiconductor to the redox-active ions in the electrolyte. Understanding such interfacial charge transfer rates is important not only in guiding the design of improved stabilizers, but also is critical to obtaining improved PHOTO ELECTROCHEMICAL efficiencies by enhancing the desirable "forward" charge transfer reactions while impeding the undesirable "back" reactions in the system.

Although significant advances have been made in recent years in the theoretical and experimental description of electron transfer reactions between molecular donors and molecular acceptors, relatively little attention has been devoted to the theory and experiments addressing these charge transfer processes at semiconductor/liquid interfaces. Such advances are required in order to elucidate the fundamental principles that govern the interfacial charge transfer processes that underlie the operation of all PHOTO ELECTROCHEMICAL cells. At present, a semiquantitative theory, based on an adaptation of Marcus' model for charge transfer at liquid/liquid interfaces, appears to be the only analytical model in the literature. This rather simple model treats the delocalized charge carrier as a reactant with an effective radius equal approximately to its Bohr radius, and assigns all of the solvent reorganization energy to the redox ion in the solution. Furthermore, this treatment is a purely nonadiabatic charge transfer model for carrier/ion separations in excess of the Bohr radius of the carrier in the solid. All of these assumptions can be criticized as primitive, but at present they provide the only available working analytical model available for comparison to experimental results. *Clearly, further theoretical development treating interfacial charge transfer processes from a semiconducting photoelectrode into a localized electron acceptor species in a liquid electrolyte is needed to place the theory of these processes on a firm, rigorous basis.*

In addition, there are very few experiments that have revealed the values of these charge transfer rate constants at well-defined semiconductor/liquid contacts. At steady state, in most cases the currents do not exhibit the predicted dependence on the concentration of carriers at the surface of the semiconductor or on the concentration of acceptor species in the liquid phase. This anomalous behavior has not received much attention in the literature although inspection of earlier work reveals it to be a widespread observation throughout the field. Such behavior is not well-understood and confounds efforts to examine in the general case the behavior of the interfacial charge transfer rate constant from steady-state current-voltage measurements. This non-ideal behavior must be understood in order to advance the theoretical and experimental description of the variety of semiconductor/liquid interfaces encountered in the literature. An alternative method for probing the desired interfacial kinetics is to determine the interfacial charge transfer dynamics in real time using ultrafast laser pump-probe techniques. Such measurements often must be performed on a rapid time scale, at low concentrations of absorbers, and must be compatible with having optical excitation of the photoelectrode only by the pumping beam and not also by the probing beam. *Thus, new*

experimental methods, capable of directly measuring these processes, are required to determine these rate constants experimentally. Work in both aqueous and non-aqueous solvents is potentially valuable to understanding this important process in a predictive fashion. The ultimate goal of this type of research is to develop sufficient understanding in order to predict which redox species would rapidly accept or donate charge to a given photoelectrode, in order to stabilize it in a desired (presumably aqueous) electrolyte.

A related issue involves control over the kinetics of both charge carrier types in an operating photoelectrode. The most efficient photoelectrochemical cell would have the redox species rapidly collect the photogenerated minority carriers, but would be kinetically sluggish towards collection of majority carriers. In this fashion, the majority carriers will be rejected at the solid/liquid interface, charge separation will be enhanced, and the desired efficient charge carrier flow through the cell will be effected. This type of asymmetric kinetic charge carrier collection is, however, not readily incorporated deliberately into a given system at present, because there is little understanding of the basic experimental principles that govern interfacial charge transfer in specific photoelectrochemical systems. *Efforts to achieve selective kinetic collection of minority carriers, while rejecting majority carriers, are thus an additional, promising area in need of fundamental research in photoelectrochemistry.*

Multi-Electron Transfer Processes for Generating Fuels Photoelectrochemically

One of the distinguishing features of photoelectrochemical cells relative to photovoltaics is their potential for integration of the energy conversion and energy storage functions necessary in any solar energy conversion system. Specifically, if chemical fuels (such as hydrogen and oxygen gas from water splitting, for example) can be obtained in an efficient photoelectrochemical process, then the need for an auxiliary energy storage device from systems that only produce electrical power can be obviated.

The key to efficient fuel formation is understanding multi-electron transfer processes and then using this understanding to develop efficient catalysts for these important chemical reactions. The catalysts could either be metallic or molecular in nature, as long as they can be integrated into an operating photoelectrochemical cell. Without such catalysis, however, much energy will be wasted in the production of fuels, and these fuels are necessary to achieve the storage and transport functions of an integrated energy conversion and storage system. Understanding these reactions also impacts the DOE Hydrogen program as well as various efforts in other programs in the DOE that address catalysis in chemical reactions.

Several photoelectrochemical cells have been reported to produce chemical fuels efficiently in certain systems. For example, $CuInSe_2$ produces I_2 from aqueous iodide ions with greater than 10% efficiency. If properly coupled with a metal electrode, this $CuInSe_2$ cell could produce H_2 and I_2 from aqueous HI. The stored chemical energy in the H_2 and I_2 would then be recovered at a later time, much as would be done if H_2 and O_2 gases had been obtained from a water-splitting process.

Similar results for I_2 production have been obtained for $MoSe_2$ electrodes, and for in situ electrical storage by the semiconductor alloy $CdSe_{0.65}Te_{0.35}$.

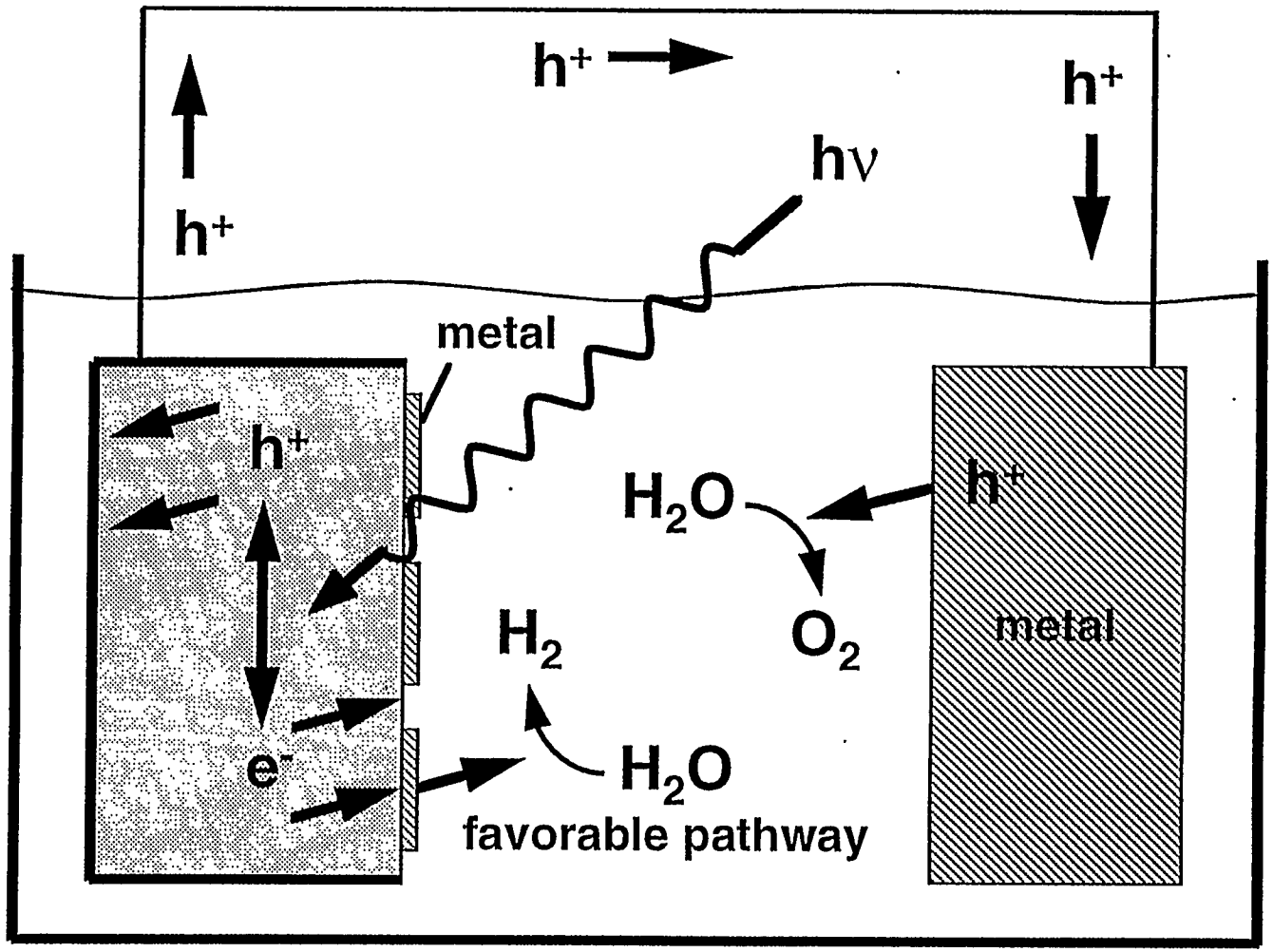
In all of these systems, evolution of I_2 is the facile fuel-forming step, because it can be readily done in a series of one-electron chemical steps. However, evolution of H_2 is a multi-electron transfer process, and will require catalytic surfaces, molecules, or noble metal electrode materials in order to be achieved efficiently. Even more severe problems arise when contemplating photoelectrochemical water splitting, in which oxygen evolution must be sustained at a low overpotential at least one electrode of the photoelectrochemical cell. *Clearly, research into catalysts for multi-electron transfer reactions that are important to fuel formation, such as oxygen from water, hydrogen from water, reduction of CO_2, etc. are critically important if efficient photoelectrochemical processes that form fuels from sunlight are to be realized.* Such systems also are of importance to maintaining high efficiency in any system which would couple photovoltaic electricity generation to an external chemical fuel formation process, such as an electrolyzer to split water into H_2 and O_2 gases, for example.

Photoelectrochemical cells using optimal solar energy absorbers such as Si and GaAs rarely provide enough output voltage to effect the unassisted production of fuels from water. Instead, the photoconversion process is used to provide a reduction in the amount of electrical power that would have otherwise been required to sustain the same chemical process. An example of this type of system is the >10 % solar energy conversion efficiency that has been demonstrated for the formation of $H_2(g)$ from water at p-type InP electrodes. In this system, the H_2 evolution was achieved by coating the photoelectrode with a catalytic, but semitransparent overlayer of metal islands (Figure 8). Such types of systems are necessary in order to lower the overvoltage for fuel formation on the photoelectrode surfaces. In a similar approach, Si electrodes have been covered with small metal islands, enabling the production of Br_2 from aqueous HBr with high efficiency. *A general approach to this problem, in which a given catalyst can be designed to enhance the rate of a desired fuel and integrated with a photoelectrochemical cell, is not currently available and is also a critical area for research in solar energy conversion.*

In addition, note that it is not generally desirable to coat the entire surface of the semiconductor with a film of a metal catalyst to achieve these fuel-forming reactions. Although such a step often minimizes corrosion and can effect the catalysis of the desired chemical fuel at the metal surface, it creates a "buried" semiconductor/liquid junction which is physically separated from the liquid. In this situation, the most optimal photovoltaic cell could be constructed and then used to provide power to an optimized electrolyzer at another location with improved efficiency and stability properties. Also, since the recombination at semiconductor/metal contacts is more rapid than that at semiconductor/semiconductor p-n junctions, these metal-coated photoelectrodes will be less efficient energy conversion devices than can be obtained from alternate methods.

A very interesting system has recently been developed which appears to avoid these drawbacks while maintaining the advantages of having a collection of catalytic sites of metal distributed over the surface of the semiconductor photoelectrode. Very small (nm-radius) metallic particles have been

Catalysis of interfacial charge transfer



Metal islands catalyze electron transfer from semiconductor

Figure 8. Use of Metal-coated Photoelectrodes in Solar-Induced Water Splitting to H_2 and O_2. a) The semiconductor absorbs light, and the photogenerated electrons are attracted to the solid/liquid interface. Metal islands deposited on the semiconductor electrode catalyze the evolution of dihydrogen gas. To complete the circuit, water is oxidized at the auxiliary electrode of the cell. When InP photocathodes are used as electrodes, the process is greater than 10% efficient at storing solar energy as H_2 and O_2 fuels.

deposited onto Si, GaAs, and other photoelectrodes, and the stability of these systems is improved significantly while they maintain the high efficiency, and excellent fuel-forming capabilities, of the semiconductor/liquid junctions and the metal/liquid junctions, respectively. *The exact mechanism of operation, and the principles by which these non-uniform, two dimensional structured overlayers facilitate the catalytic fuel-formation reactions catalysis while not inducing excessive surface recombination remains uncertain and appears to provide a very promising avenue for further research efforts.*

Surface Modification of Semiconductor Electrodes

In addition to searching for new bulk materials to obtain efficient, stable, photoelectrodes, it is also possible to envision modifying the surface of existing materials in order to improve their chemical stability as well as to improve their energy conversion efficiencies. Surface modification can be used to effect improved photoelectrode stability if it can be used to direct the photogenerated charge carriers towards desired reactants instead of towards those involved in the undesired passivation or

corrosion steps. In addition, the dominant site of charge carrier recombination in many semiconductor photoelectrodes is at the solid/liquid interface. Thus, even stable cells may not be optimally efficient solar energy conversion devices unless suitable surface modification processes can be identified and incorporated into the cell design.

The role of surface modification in improving photoelectrode stability has been well-documented in several systems, including Si electrodes modified with ferrocenes, GaAs electrodes coated with conducting organic polymers, and other such groups. In many systems, however, the basic surface chemistry is not sufficiently well-understood to allow a rational approach to modification of a semiconductor photoelectrode. Functionalization of such surfaces is currently done on an "ad-hoc" basis with little control over the overlayer chemistry or the stability of the linking group to the surface, precluding both rational design of the system and long term stability of the overlayer in an operating photoelectrochemical cell environment. Linkages to catalysts for fuel-formation, to stabilizing redox groups, to protective overlayer structures, etc., cannot be generally formed unless the surface chemistry of the semiconductor is well-understood. *Therefore, research focused towards identifying and exploiting the chemically reactive functionalities of important semiconductor photoelectrodes, as well as research into methods that will allow the synthesis of overlayers of designed composition and structure, are important components of a research program in photoelectrochemical energy conversion.*

Surface modification is also important in order to improve the electrical properties of etched semiconductor surfaces. In general, the bonds at the surface of a semiconductor are not as strong as those in the bulk, so the band structure that characterizes the bulk solid is not preserved at the solid/liquid interface. The atoms at the surface of the solid therefore often act as electrical traps, and induce efficient charge carrier recombination that is deleterious to the energy conversion efficiency of the photoelectrochemical cell. Even electrical defect densities as low as 1 in every 100 surface atoms can severely hamper the energy conversion efficiency of the photoelectrochemical device.

Any surface modification procedure must not create significant electrical defect densities at the semiconductor surface, otherwise the benefits of control over the chemical properties of the surface will be mitigated by the reduced energy conversion efficiencies of the resulting photoelectrochemical device.

Relatively few efforts have been directed at investigating the fundamental chemistry of etched photoelectrode surfaces to achieve these goals. Some work has emerged on GaAs, Si, and InP electrodes, but little is understood beyond these few systems. For example, until recently, no chemical functionalization processes were known for the H-terminated Si surface that forms the basis for photovoltaics, photoelectrochemical cells, and modern electronic Si device fabrication. This effort also needs development of new methods of characterizing these surfaces so that they can be defined and understood in a method that allows further manipulation in a rational fashion. Examples of such new tools would include light-induced photocurrents probed locally by scanning probe microscopy and other recently developed in-situ methods for probing the solid/liquid interface. *Efforts directed at elucidating the chemistry of important photoelectrode surfaces, especially with respect to controlling simultaneously their electrical and chemical properties, are critical to obtaining the surfaces needed for efficient photoelectrochemical energy conversion systems from small band gap semiconductors, as are methods for characterizing these interfaces in situ and on a local, molecular resolution length scale.*

Hot Carrier Capture for Fuel Formation and Elucidation of the Energetics of Junction Formation at the Semiconductor/Liquid Contact

Another potential advantage of semiconductor/liquid contacts involves the utilization of unthermalized "hot" carriers to effect fuel-forming photoelectrochemical processes. If the photogenerated carriers could be harvested to form chemical fuels before they produced waste heat during the thermalization process in the semiconductor, significantly improved energy conversion efficiencies might be obtained. In fact, it has been estimated that efficiencies of up to 50% could be achieved through this approach. *Since these improvements in efficiency are very significant, it seems prudent to explore the opportunities, both theoretically and experimentally, for the use of hot carriers in improving the efficiencies, in a unique fashion, of photoelectrochemical cells relative to alternative solar energy conversion technologies.*

Collection of hot carriers requires very rapid interfacial charge transfer events as well as an increase in the thermalization times for carriers in the bulk of the solid. It is thus important to understand the factors that control interfacial charge transfer, as discussed above, in order to quantify the yield of hot carriers that can be expected for particular choices of semiconductors and electrolytes. Experiments designed to probe these carrier dynamics are therefore timely and highly desirable. In addition, a complete theoretical analysis of an operating system, outlining how the hot carrier collecting chemical reactions would be separated from the thermalized carrier collection reactions and other thermodynamics and dynamics of an optimized system, also would seem warranted at present.

A closely related issue involves prediction of the energetic properties of a semiconductor/liquid contact. At present, the energies of the band edges, and thus the driving force for charge transfer events, recombination events, and other key properties of a photoelectrochemical cell are determined empirically for each semiconductor/liquid contact of interest. Theoretical methods of predicting these energetics, and a coupled experimental validation of these predictions, would be of great use in selecting potentially optimal choices for photoelectrochemical energy conversion devices.

Photoelectrochemical Cells Using Polycrystalline Semiconductors or Thin Film Semiconductors

Another demonstrated advantage of photoelectrochemical cells is the ability to effectively utilize relatively inexpensive, polycrystalline semiconductor materials with efficiencies that are comparable to those obtained using more expensive single crystal semiconductor materials. The main reason for this advantage relative to solid state photovoltaic cells is that formation of a solid/solid junction on a rough, nonhomogeneous interface is difficult whereas the liquid conforms naturally to any topographic variations in the semiconductor surface and makes a well-defined electrical contact to this type of material. For example, photoelectrochemical cells made from polycrystalline GaAs, CdSe, other semiconductors have retained a remarkable 80% of the efficiency of their single crystal semiconductor/liquid contact counterparts. This potential advantage of photoelectrochemical solar energy conversion devices should continue to be explored and exploited whenever possible, especially with respect to recent advances in this area in the metal oxide nanocrystalline phases as well as with other semiconducting materials of small particle size. Note that this line of research runs contrary to that of the photovoltaic community, in which extensive, costly efforts are made to fabricate material of high purity and large grain size to reach high efficiencies; in photoelectrochemical cells, small grain size materials appear to be advantageous in certain systems and these advantages should be explored further in future research.

A related issue relates to grain boundary passivation processes in the polycrystalline films of semiconductor/liquid contacts. Just as was the case for surfaces of single crystal photoelectrodes, the surfaces of polycrystalline materials exposed at grain boundaries often serve as recombination sites or as barriers to transport of photogenerated carriers through the film to produce current in the device. Chemical methods for passivating these grain boundaries have been demonstrated in a few systems to date, but the basic chemistry that is occurring in these systems is not well-understood at present. *Studies designed to elucidate the chemistry of grain boundary sites, to control their electrical properties, and to reduce barriers to carrier transport across grain boundaries, are therefore of great interest to obtaining low cost, high efficiency photoelectrochemical energy conversion devices.* This area could potentially have an enormous impact in placing photoelectrochemical energy conversion devices into a favorable region of the cost/efficiency curve relative to solid state photovoltaic devices and deserves significant attention from the research community and transfer to technological devices if successful.

New methods for preparing nanocrystalline semiconductor thin films should also be investigated. Materials characterization issues related to these films, such as various interfacial properties (e.g.,

interfacial pH, electric field distribution, etc.) must also be characterized if these films are to be compared from laboratory to laboratory and investigated in a rational fashion. This will require development of new experimental methods and/or exploitation of emerging methods (for example, second harmonic generation or sum frequency generation) to access the important interfacial parameters in these spatially nonuniform thin film devices. *The nanocrystalline thin films present exciting opportunities at the interface of materials chemistry, colloid science, and device physics, and should be a significant component of an ongoing research program in photoelectrochemical energy conversion.*

Historical Perspective and Accomplishments in the Field

Photoelectrochemistry has already had a significant impact on a number of fields and has led to new technologies as well as to spin-off technologies in a variety of areas. Photocorrosion, which is the bane of stable photoelectrochemical solar energy conversion devices, has been exploited to prepare technologically useful structures such as lenses integrated with light emitting diodes and their mated optical fibers. It has also led to the formation of porous Si electrodes which have received much attention in the past few years due to their interesting optoelectronic properties. Photoelectrochemical surface preparation of semiconductor materials has been used to clean solids, to evaluate their etch pit densities, and has been used in electroplating metal contacts onto desired areas of integrated circuits. In addition, a commercial device for profiling the chemical composition and dopant concentration of semiconductor heterostructures used in lasers, light emitting diodes, advanced microwave devices, etc. has been developed and is widely used in the research and manufacturing community. The entire field of photochemical waste treatment using titanium or other semiconducting metal oxides was a spin off from basic research in semiconductor photoelectrochemistry of interest to solar energy conversion. Light addressable potentiostatic sensors, based on the chemistry of the Si/liquid interface developed in photoelectrochemical studies, have been commercialized for use as biosensors, enzymatic assays, and even as low power, portable chemical warfare agent detectors.

Photoelectrochemistry has also led to a set of methods for the nondestructive characterization of the bulk and surface properties of various semiconducting materials. The identification of stable electrode/electrolyte combinations has enabled use of the Mott-Schottky (differential capacitance vs. voltage) methods, which were first used on solid-state junctions, to be applied to the nondestructive measurement of the flat band potentials and dopant densities of solids. Photocurrent spectroscopy has led to methods for rapid measurement of the band gaps and related optical properties of solids, as well as for the detection of surface states and their electrical characterization. In situ electroluminescence and photoelectroluminescence measurements have been developed to probe bulk and surface recombination sites in various semiconductors, and to provide quality control checks and convenient, reliable monitors of semiconductor wafer quality.

In parallel with the development of these applications, significant progress has been made towards the basic goal of understanding the operation of, and improving the stability and efficiency of, photoelectrochemical energy conversion devices. A decade ago, few examples existed of

photoelectrochemical cells with solar energy conversion efficiencies in excess of 10%, whereas examples of such systems abound at present. No theory was available to describe interfacial charge transfer rates, and now experiments are being performed to evaluate key parameters in the operation of such systems. Nanocrystalline electrodes and dye sensitized semiconductor photoelectrodes were just a laboratory curiosity a few years ago, but have now emerged amongst the most promising systems for combining low cost, high efficiency, and high stability into a readily manufactured solar energy conversion device. Thus, although much remains to be done to gain a full understanding of the semiconductor/liquid contacts, the progress in the past few years has demonstrated that these systems can afford real, reproducible, efficient solar energy conversion devices that have significant promise for providing an option to produce renewal energy on a wide scale from the sun.

Summary and Recommendations

Although photoelectrochemical cells are simple to fabricate, straightforward in concept, and have been demonstrated to produce extremely high solar energy conversion efficiencies, photoelectrochemical systems present a number of scientific and engineering challenges in conjunction with their potential implementation as widely adopted, fieldable energy conversion devices. These challenges include:

- improving the stability of photoelectrochemical cells, especially those operating in aqueous electrolytes;
- improving the efficiency of desirable photoelectrode/electrolyte combinations through chemical control over the bulk and surface properties of the solid and control over the composition of the electrolyte;
- discovering new semiconducting materials or surfaces with desirable properties, such as significantly reduced manufacturing costs, increased efficiency in water photoelectrolysis applications and improved stability in certain desirable electrolytes.
- discovering new catalysts to enable the energy-efficient multi-electron transfer reactions necessary for photoelectrochemical fuel formation.

Specific areas of promise and importance for a thorough, balanced research program in photoelectrochemistry can be summarized as follows:

- New materials are required in order to obtain photoelectrodes having the right band gap and stability properties in aqueous solution.
- Research into the underlying, fundamental mechanisms by which semiconductor electrodes corrode or passivate in aqueous solutions, and into mechanisms for competing successfully with these undesirable reactions, also could potentially have great impact in advancing photoelectrochemical energy conversion.

- Further theoretical developments treating interfacial charge transfer processes from a semiconducting photoelectrode into a localized electron acceptor species in a liquid electrolyte are needed to place the theory of these processes on a firm, rigorous basis.

- New experimental methods, capable of directly measuring interfacial charge transfer processes, are required to determine these fundamentally and practically important rate constants experimentally.

- Efforts to achieve selective kinetic collection of minority carriers, while rejecting majority carriers, are thus an additional, promising area in need of fundamental research in photoelectrochemistry.

- Research into catalysts for multi-electron transfer reactions that are important to fuel formation, such as oxygen from water, hydrogen from water, reduction of CO_2, etc. are critically important if efficient photoelectrochemical processes that form fuels from sunlight are to be realized.

- A general approach is needed in which a catalyst designed to enhance the rate of a desired fuel and integrated with a photoelectrochemical cell can be selected.

- The exact mechanism of operation, and the principles by which non-uniform, two dimensional, structured overlayers consisting of nanometer-sized metal particles facilitate the catalytic fuel-formation reactions catalysis while not inducing excessive surface recombination remains uncertain and appears to provide a very promising avenue for further research efforts.

- Research into identifying and exploiting the chemically reactive functionalities on important semiconductor photoelectrodes, and into methods that will allow the synthesis of overlayers of designed composition and structure, is an important component of a research program in photoelectrochemical energy conversion.

- Efforts directed at elucidating the chemistry of important photoelectrode surfaces, especially with respect to controlling simultaneously their electrical and chemical properties, are critical to obtaining the surfaces needed for efficient photoelectrochemical energy conversion systems from small band gap semiconductors, as are methods for characterizing these interfaces in situ and on a local, molecular resolution length scale.

- It seems prudent to explore the opportunities, both theoretically and experimentally, for the use of hot carriers in improving the efficiencies, in a unique fashion, of photoelectrochemical cells relative to alternative solar energy conversion technologies..

- Studies designed to elucidate the chemistry of grain boundary sites, to control their electrical properties, and to reduce barriers to carrier transport across grain boundaries, are of great interest to obtaining low cost, high efficiency photoelectrochemical energy conversion devices.

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Photochemical Solar Cells and Photosensitization Processes

Status and Issues

Recent reports of high efficiency photochemical solar cells have raised expectations of the imminent development of commercially viable solar cells (1-5). In these cells the photoresponse of a large bandgap semiconductor (E_g>3.0 eV) such as TiO_2 is extended into the visible region by modifying the semiconductor surface with a sensitizing dye such as ruthenium (II) polypyridyl complex. Upon excitation with visible light the sensitizing dye molecules inject electrons into semiconductor nanocrystallites which are then collected at a conducting surface to generate photocurrent. The principle of a nanocrystalline semiconductor based photochemical solar cell is illustrated in Figure 1.

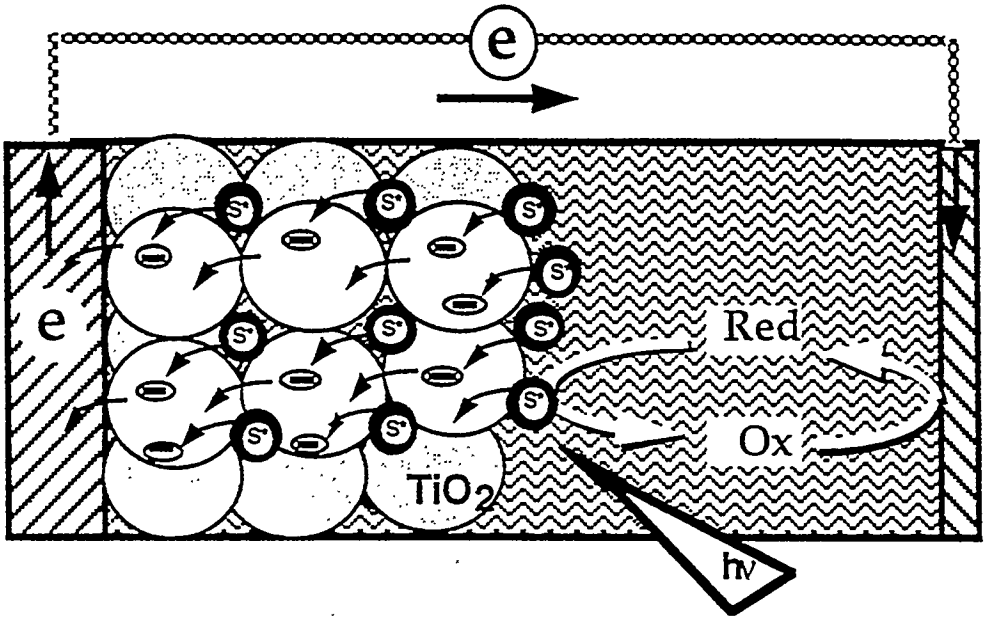


Figure 1: Photoinduced charge transfer processes in a Photoelectrochemical solar cell.

The process of utilizing subbandgap excitations with dyes is referred as photosensitization and is also employed in color photography and other imaging science applications. This approach of light energy conversion is similar in many respects to plant photosynthesis, in which chlorophyll molecules act as light-absorbing antenna molecules. In other words, the dye-modified semiconductor films provide an efficient method to mimic the photosynthetic process. The nanostructured TiO_2 films modified with ruthenium complexes exhibit 7-10% photoconversion efficiency which is comparable to that of amorphous silicon-based photovoltaic cells and over twice the efficiency of natural photosynthesis.

Three important processes control the efficiency of incident photon-to-charge carrier generation. They include (i) the primary photochemical event of charge injection from excited sensitizer into semiconductor nanocrystallites, (ii) charge transport across the nanocrystalline film and (iii)

regeneration of sensitizer with a suitable redox couple. To date little is known about the kinetics and mechanistic details of these important photochemical and photoelectrochemical processes.

How quickly does photoinduced charge transfer occur on semiconductor nanocrystallites? One common method to probe the kinetics of charge injection process is to monitor the luminescence decay of the sensitizer on the semiconductor surface. The charge injection can occur from both excited singlet (S_1) and triplet (T_1) excited state as illustrated in Figure 2.

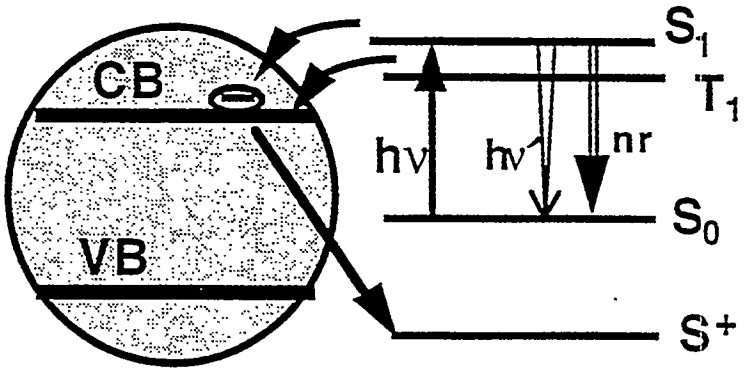


Figure 2: Excited state processes of a sensitizing dye molecule adsorbed on a semiconductor nanocluster

It has been reported (6,7) that charge injection from excited singlet state is an extremely fast process and completes within picoseconds at low submonolayer coverages on the semiconductor surface. In the case of phosphonated perylene derivatives the charge injection is completed within 500 fs. High surface coverage of the dye employed in photoelectrochemical cells for maximizing the light harvesting efficiency and differing experimental conditions often influence the charge transfer kinetics. Nonradiative processes such as excited state annihilation, ground state quenching, energy transfer to surface or surface impurities can compete with the heterogeneous electron transfer. Therefore, luminescence decay alone cannot yield complete information regarding the charge injection process.

Recent lifetime measurements of Ru(II)-complex modified SnO_2 and TiO_2 nanocrystallites have shown that the charge injection process occurs with a rate constant in the range of 10^8-$10^{10}s^{-1}$ (8-10) Emission decays in these studies typically are multiexponential implying the existence of nonhomogeneous injection and/or adsorption sites on the semiconductor surface. Trapping and detrapping processes can also play a major role in influencing the kinetics of the charge injection process. Methods such as photoelectron spectroscopy, microwave conductivity and quartz crystal microbalance are especially suited for *in situ* electrochemical and photochemical experiments. The dye/TiO_2 interface as well as cation-insertion in nanostructured TiO_2 electrodes have been studied with quartz microbalance (11), XPS and synchrotron radiation (12). Complementary quantum chemical calculations have shown good correlation with the experiments, giving further insight into the electronic structure of the systems studied. The sensitization aspects of monomeric and

aggregate forms of organic dyes have been extensively investigated, but the low energy conversion efficiency is still an intriguing problem.

What are the Controlling Factors? The energy difference between the conduction band of the semiconductor and oxidation potential of the excited sensitizer is the major driving force for the excited state charge transfer. A simple energy level diagram is illustrated in Figure 3.

A variety of approaches have been considered to establish the energy gap dependence of the photosensitization efficiency (13-18). Resonance Raman spectroscopy (19) and transient absorption spectroscopy (20,21) have been successfully employed to monitor the photochemical changes that occur at the nanocrystalline semiconductor surface under the influence of an externally applied electrochemical bias. Since the pseudo-Fermi level of the SnO_2 nanocrystalline film can be varied by an externally applied electrochemical bias it is possible to alter ΔE and hence the kinetics of heterogeneous electron transfer. With increasing ΔE one sees efficient quenching of the sensitizer by the semiconductor. The energy gap also depends on medium pH since the conduction band of metal oxide semiconductor shifts 59mV per pH unit.

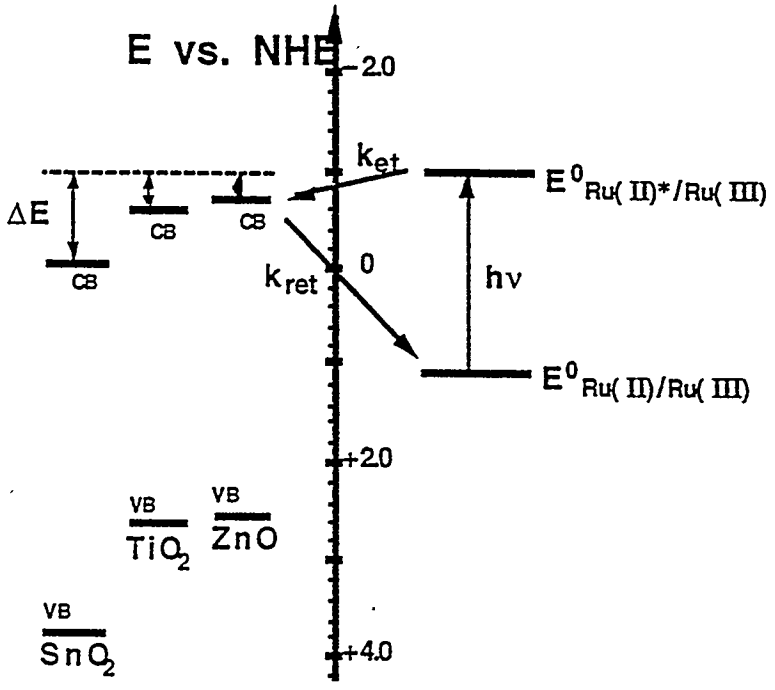


Figure 3: Energy level diagram of semiconductor and redox potentials of sensitizer.

Another important aspect is the properties of semiconductor nanoclusters that collectively control the photoelectrochemical behavior of the semiconductor thin film (22). These thin films can be designed using chemical precipitation (23) and electrochemical deposition methods (24). Examples of composite semiconductor nanoclusters with capped and coupled geometry are illustrated in Figure 4.

Since these composite semiconductor films are photoelectrochemically active it opens up a wide array of possibilities in utilizing these materials for a variety of different applications (23). The advantage of using composite semiconductor films in photoelectrochemical cells is twofold: (i) to extend the photoresponse by coupling a large-bandgap semiconductor with a short-bandgap semiconductor (25-27) and (ii) to retard the recombination of photogenerated charge carriers by injecting electrons into the lower lying conduction band of the large bandgap semiconductor (28) The use of such semiconductor heterostructures in dye-sensitized photochemical solar cells has yet to be explored.

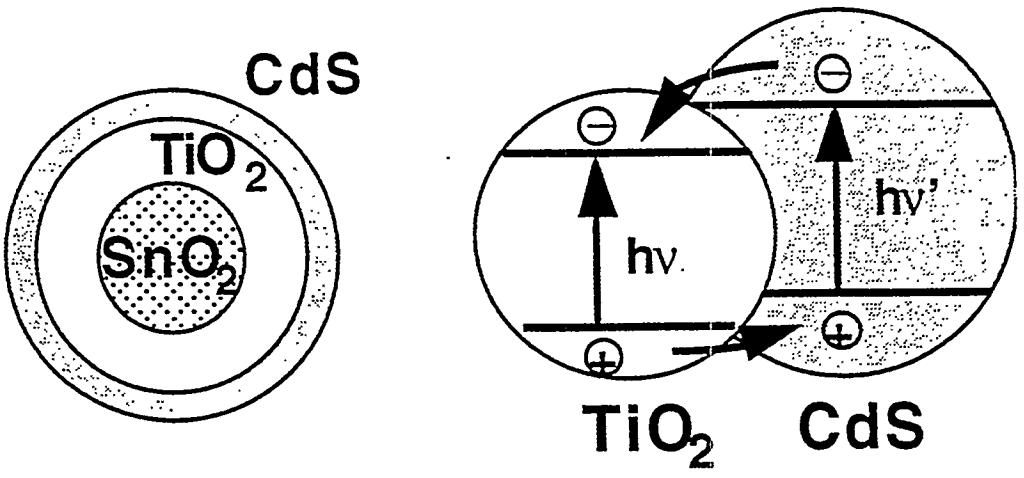


Figure 4: Composite semiconductor nanoclusters with capped (left) and coupled geometries

Although nanocrystalline semiconductor films cannot form a Schottky barrier, a potential gradient arising from varying degrees of electron accumulation within the semiconductor particles apparently acts as a driving force for the transport of electrons across the film (28-30). A diffusion model has been attempted to explain the charge transport in nanostructured semiconductor electrodes (31). Efforts are currently underway in several laboratories to explore the mechanism of charge transport within the nanocrystalline film and to obtain the kinetic details of the charge injection process.

Reverse electron transfer between the injected charge and the sensitizing dye is a process that results in recombination losses (20,32). It can be conveniently monitored from the recovery of the sensitizer or from the decay of oxidized sensitizer. The reverse electron transfer is a multiexponential process with a range of rate constants and suggests inhomogeneity of trap and/or surface sites that control the heterogeneous electron transfer. For Ru(II) complexes the reverse electron transfer rate constant is 3-6 orders of magnitude lower than the rate constant of the charge injection process. Incomplete regeneration can also lead to the permanent destruction of the sensitizer. The regeneration of sensitizer with a redox couple is important for achieving maximum efficiency and long-term photostability.

Future Goals and Challenges

The major competitive barrier for photochemical solar cells is the lower power conversion efficiency compared to existing photovoltaic technology. In organic dye-based cells, this efficiency is less than 1% while in Ru(II) polypyridyl complex based systems it is around 7-10%. The ultimate goal would be to improve the efficiency of photochemical solar cells to at least 15-20%. Photodegradation of such dye-sensitized devices can also be an important factor in the long-term stability of these cells. These barriers can only be overcome with a thorough, balanced program of fundamental research in photochemistry. *The major research efforts should include characterization of excited state properties of the sensitizers, photoelectrochemical behavior of nanocrystalline semiconductor films, elucidation of the mechanistic and kinetic details of heterogeneous electron transfer at the dye-semiconductor interface, intermolecular interaction between photoexcited dye molecules on semiconductor surface and photostability of sensitizing dyes and semiconductor nanoclusters.* Specific details of the experimental and theoretical approaches are summarized as follows.

Design and Characterization of Nanostructured Semiconductor Films

An important aspect of operating an efficient photochemical solar cell is to synthesize nanostructured semiconductor films with high surface area and an optimum pore size. *It will be necessary therefore to focus future efforts towards controlling the morphology of nanostructured semiconductor films so that packing and porosity are optimized.* One way to achieve this goal is to synthesize monodisperse sols of a wide range of semiconductor materials. The preparation of gels from the above sols will, in turn, permit preparation of a wider range of supported nanoporous-nanocrystalline semiconductor films. Improvement in sol-gel synthesis of nanostructured semiconductor material should also be attempted.

Two other general approaches should be explored. First, a top-down approach in which a single crystal is processed to yield a nanoporous crystalline material of a well-defined morphology. A similar effort has already been made in developing luminescent silicon nanocrystallites by single crystal etching (33). Photoelectrochemical etching may also be useful for making layered-type semiconductors highly porous (34). Second, a bottom-up approach in which nanocrystallites are organized to yield a nanoporous-nanocrystalline materials of a required morphology. For the latter approach, successive deposition of ordered monolayers of nanocrystallites using Langmuir-Blodgett techniques or by self-assembly is contemplated (35). Contemporary with the above will be the development of improved techniques (e.g., Scanning electron microscopy (SEM) as well as X-ray diffraction (XRD) and X-ray Photoelectron spectroscopy (XPS)) for structural characterization of the resulting ordered nanoporous-nanocrystalline materials. Such designed nanoporous-nanocrystalline materials would also represent a necessary step in the development of a detailed physical model for transport processes within such materials.

Composite semiconductor thin films made up of two or more semiconductor nanocrystallites should also be explored for dye sensitization systems as they are known to improve charge separation. The ability to self-assemble nanocrystalline architecture of desired morphologies, linked to recent

developments in supramolecular photochemistry, offers exciting opportunities for both fundamental and applied studies.

Photoelectrochemical Properties of Nanostructured Semiconductor Films

At present, little is known about the photoelectrochemical behavior of nanocrystalline semiconductor films. Despite the fact that the nanostructured semiconductor films do not possess an ideal space charge layer, the i-V characteristics and other photoelectrochemical measurements indicate these films behave similarly to that of polycrystalline semiconductor materials. However, other findings suggest the possibility of a fundamentally different underlying physics. *The obvious need therefore is to obtain a scientific explanation that can describe the charge distribution, charge transport, charge collection processes in these closely packed semiconductor particulate films.* Both theoretical modeling and photoelectrochemical measurements have to be carried out. Of particular interest are the origin of collective phenomenon and correlation of single particle charge transfer properties with macroscopic properties through the morphology of device.

Other important issues that need to be addressed include charge transport mechanism (surface vs. bulk, hopping, tunneling), role of surface states or grain boundaries (energy, density, chemical nature), potential distribution across the film under illumination, adsorption/desorption mechanism (dyes, passivation, reagents, etc.). Development of more elaborate charge transport models integrating facts of electrolytes, traps, recombination, etc. (dispersive transport models) should also be considered.

Understanding the Operation and Optimization of Photochemical Solar Cells

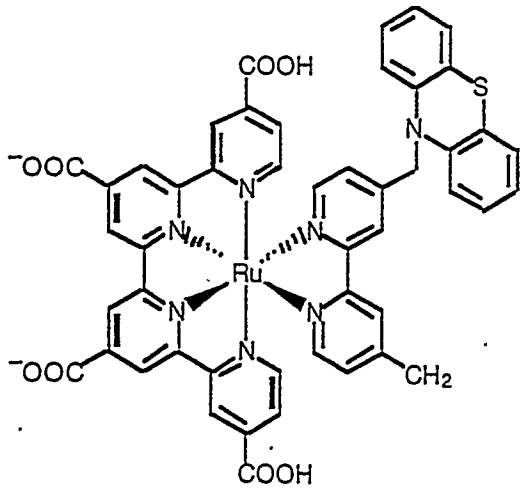
Photochemistry and Photophysics of New Sensitizers

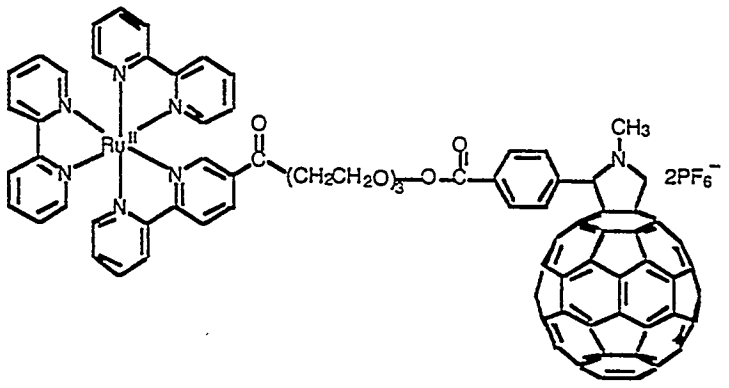
Stable molecular sensitizers which efficiently harvest a large fraction of sun-light are needed for the development of an efficient solar cell. The most promising sensitizers to date are based on Ru(II), Os(II), and Re(I) polypyridyl compounds. New compounds and the development of efficient synthetic routes to their preparation are required. *Fundamental studies of solution photophysics, stability and redox reactions are needed. Molecular methods for anchoring and orienting the sensitizers to semiconductor oxide surfaces and spectroscopic characterization of the linkage require further development.* Alternative molecular sensitizers based on organics, metal cyanides, porphyrins, and phthalocyanines should be developed. Ideally these sensitizers should strongly absorb visible light, and be stable in the oxidized, reduced and excited states.

Although dye aggregates have been shown to be effective in imaging science applications, they exhibit relatively low efficiency as compared to Ru(II) polypyridyl complexes for sensitized photocurrent generation. The strong absorption of organic dyes in the red and IR region, however, suggests they should be considered further as photosensitizers and that attention be focused in overcoming the problems associated with aggregation. A few preliminary investigations have been carried out to understand the photosensitization property of dye aggregates of cyanine and oxazine

dyes adsorbed on semiconductor nanoclusters. There is a need to elucidate the excited state dynamics of these sensitizer materials so that one can clearly understand the limitations of organic dyes as photosensitizers.

Supramolecular sensitizers composed of covalently linked donor-acceptor moieties which promote efficient charge separation deserve careful consideration. Examples of such supramolecular assemblies are illustrated below (36-39).





Polynuclear antenna sensitizers which harvest visible light and vectorially translate the energy toward a central component capable of injecting electrons into wide band gap semiconductors, will perhaps allow the use of thinner porous nanocrystalline films. Such an approach is likely to decrease the losses associated with carrier transport through thick films. Sensitizers which are comprised of a chromophoric donor with a pendant electron donor would allow the sensitizer to be regenerated intramolecularly. Such systems can inhibit electron recombination by translating the hole away from the interface thereby increasing the open circuit voltage of the device. Photoinduced concentration gradients of redox species in the film (diffusion coefficients of the redox system) also need to be addressed.

Theoretical efforts should be directed towards developing models for molecular dynamics calculations of dye orientation and interaction with oxide surfaces, electronic coupling between the dye and semiconductor surface.

Photochemistry of Semiconductor Nanoclusters

The photochemical and photophysical study of semiconductor nanoclusters is another important area of research that needs careful attention. *Efforts should be made to correlate the properties of the nanoclusters with the physics of quantum dots.* Of particular interest are the optical and dielectric properties and interparticulate charge screening.

Although a few efforts have been made to synthesize semiconductor composites with capped and coupled geometries, photoinduced charge separation in such systems is not fully understood. Since these multicomponent semiconductor nanoclusters facilitate improved charge separation it is necessary to carry out systematic evaluation of photophysical and photochemical properties.

The use of nanometer semiconductor particles as sensitizers in place of dye molecules will depend critically on whether one can avoid traps in the bulk and at the surface of the semiconductor particles. Use of short band gap semiconductors as sensitizers hold the promise of greater stability.

Energetics, Kinetics, and Dynamics

The energetics of the involved electronic states can be obtained from dynamics, electrochemical measurements and photoelectron spectroscopy. The sequence of all the electron transfer steps comprises the overall kinetics. The system has to be designed such that the incident photon-to-charge carrier conversion efficiency (IPCE) is higher than 90%. This is achieved when all forward reaction steps are about 100 times faster than the competing reaction steps such as deactivation and recombination. Time resolution of the initial charge injection steps requires femtosecond-picosecond methods. To achieve long term stability the forward reaction steps must be 10^6 times faster than irreversible degradation steps. The energy difference required for the individual reaction steps increase with the reorganization energy. Therefore, a device based on *all solid state* system may be advantageous and such systems certainly should be explored. Dynamics of the reaction steps comes from time-resolved, energy-resolved, and temperature dependent measurements. *Questions still remain concerning the lack of responsiveness of ultrafast charge injection kinetics (at least in some systems) to large changes in band location. Again the fundamental basis for these observations needs to be understood if devices are to be fully optimized.*

Other points that need to be scrutinized include the effect of the Helmholtz layer potential on the dynamics of the injection, recombination and regeneration step involving the sensitizer. and the effect of Li^+ or H^+ ion intercalation on the surface charge and position of the conduction band.

Recombination Reactions and Losses

Stability of PV cell operation

The question of cell stability was discussed in particular with regard to dye cycle life. To reach a turnover number of 10^8 required for continuous cell operation for 20 years it was agreed that fast regeneration of the currently used ruthenium(II) complex sensitizer following the electron injection event was very critical. This process should be completed within 10 to 20 nanoseconds to obtain the desired cycle life given the fact that the lifetime of the oxidized state in the absence of a regenrative system is in the millisecond to second domain. A quantitative description of the sensitizer regeneration is therefore essential for understanding the photostability issues.

Back Electron Transfer

Recombination kinetics (back electron transfer kinetics) largely defines the magnitude for a key branching ratio necessary for efficient solar energy conversion in any dye-sensitized cell. An apparently unique or nearly unique characteristic of metal-oxide semiconductor/dye systems is moderately slow back ET which permits comparatively efficient cell operation. Slow back ET is particularly remarkable in view of fast forward ET (dye injection) in the systems discussed above. *Rational optimization and generalization of these fortuitous findings require the elucidation of mechanisms for both processes and the development of a fundamental understanding of the relationships between mechanism and reactivity, on the one hand, and molecular structure and materials structure, on the other.* Among the specific issues that need to be resolved are: (i) the role of recently discovered intercalation and photo intercalation events, (ii) the role of overall reaction energetics versus isolated ET energetics, (iii) the applicability/transferability of key molecular reactivity concepts such as (non)adiabaticity, solvent polarization/reorganization and Franck-Condon factors (vibrational overlaps), (iv) the role of surface structure and surface electronic states, (v) the mechanistic validity/usefulness of conventional band structure concepts at nanocrystalline semiconductor/solution interfaces, (vi) the mechanistic basis for ultimate trade-offs between broad spectral coverage and both injection and recombination kinetics/dynamics, and (vii) the extent to which supramolecular assemblies can be used to enhance separation efficiencies. Also needed is further development of powerful new spectroscopic and related methodologies that provide real-time descriptions of dynamics, transient electric field effects, coupled ion transfer effects, molecular vibrational effects.

Establishing Photodegradation Pathways for the Dyes Adsorbed on Semiconductor Surfaces

The intrinsic property of the support material plays an important role in controlling the excited state behavior of sensitizing dyes. Sensitizers adsorbed on large bandgap semiconductors undergo

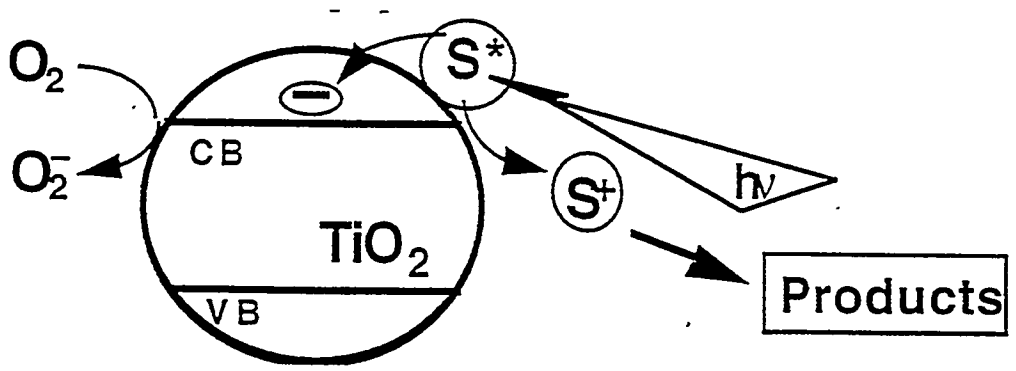


Figure 5: Photochemical degradation of sensitizing dye on TiO_2 particle.

photooxidation following the charge injection event if they are not quickly regenerated with a suitable electron donor (9). A schematic illustration of this degradation pathway is illustrated in Figure 5.

Alternatively direct band gap excitation of semiconductor with UV-light might also lead to photodegradation. The excited state photochemistry of the sensitizer in the absence of a regenerative system will provide some important information about the kinetics and mechanism of photochemical processes on semiconductor surfaces. *The steady state photolysis and analysis of the photoproducts are necessary to identify the photodegradation pathways.*

New Areas Relevant to Technology

Thin nanostructured semiconductor films have important technological applications in chemical sensors, microelectronics, electrooptics, imaging science, and storage batteries. Chemical vapor deposition or molecular beam epitaxy has been the preferred technique for depositing thin semiconductor films. Compared to these ultrahigh vacuum deposition techniques chemical and electrochemical approaches of casting thin films are relatively simple and inexpensive. Another area that can benefit from the photochemical understanding of nanostructured semiconductor film is the area of photocatalysis. One such example would be to use a photosensitization approach for degrading colored contaminants such as textile dyes over semiconductor particulate systems. The information of dye degradation on semiconductor surface will also be helpful in improving the photostability of TiO_2 based paints and other pigments. The nanostructured semiconductor films also provide a convenient way to carry out bimolecular reactions in a confined reaction space of the nanopores.

Summary

The basic principle of the photochemical devices described above essentially involves photochemical reaction at the dye/semiconductor interface. A complete understanding of photochemical processes of sensitizers adsorbed on semiconductor nanocrystallites is therefore crucial for developing highly efficient photochemical solar cells. In order to understand the operation and optimization of photochemical solar cells it is necessary to elucidate energetics, kinetics and dynamics of sensitizer-semiconductor systems. Efforts should also be directed towards the design and characterization of various semiconductor nanoclusters, semiconductor heterostructures and supramolecular sensitizers. Theoretical and experimental approaches have to be simultaneously developed to model the charge carrier transport and potential distribution within the film. This is a fundamental science of great importance and strong support by the Department of Energy is recommended.

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Organic Solar Cells and Other Photoconductive Systems

Organic Solar Cells

Early work with organic molecules in solid state energy transduction focused on Schottky barrier solar cells (1,2). Metal contacts were evaporated onto films of organic dyes, that included examples of cyanine, merocyanine, phthalocyanine and xanthene dyes. Although the extinction of the cells in the visible was high, charge transport across the organic layer and its collection at the contacts kept the conversion efficiency down. The maximum reported power conversion efficiencies for organic molecular solar cells were found to be 1% at AM 1.5.

In an advance from the Schottky barrier configuration, a new form of photovoltaic cell has been made in with pairs of organic dyes evaporated sequentially in layers to form a junction (3). Belonging to the phthalocyanine and perylene classes, the dyes were chosen for high stability and chemical resistance and survive a sublimation at 400-500 C. These dyes are also used in Xerographic photoreceptors. The complementary absorption of the dye pair results in a high extinction from 400-700 nm with a total thickness of 500-600 A of deposited dye. These systems are entirely solid state with ITO front surface layers and evaporated metal back contacts. Fill factors can be limited by high bulk resistance, high contact resistance or by the bias dependence of quantum efficiency in systems where the first two have been addressed. A present measure of performance of these cells is their 20% quantum efficiency using monochromatic radiation. This work has uncovered the deleterious impact of impurities upon charge separation and transport within the dye layer. An improvement in cell performance is expected when impurities in the dye are removed.

The importance of highly ordered films has been demonstrated by studying liquid crystalline porphyrins which self-assemble into highly ordered lattices upon coating (3-6). They are inserted into a symmetric cell where the chromophore is oriented between ITO contacts in a liquid crystalline arrangement forced by substituents on the porphyrin. Photocurrents, photovoltages, and exciton diffusion lengths are found to improve with increasing film order. The exciton generated by light absorption dissociates to generate charge; this can happen in the bulk or at either of the contacts, and the rate may be different at the dark contact as opposed to the illuminated contact.

Neither of these formats for organic molecular solar cells, the junction arrangement or the liquid crystalline arrangement, has been subjected to extensive stability tests, which are more suitable for higher yield devices.

Other Photoconductive Systems

The fundamental research problems in molecular organic cells, photoelectrochemical cells, and dye-sensitized cells overlap strongly with that of other, non-energy technologies. It is evident that specific areas of research in these topics have direct relevance to energy technologies and their investigation yields results of direct benefit to solar photoconversion systems.

Molecular organic photoreceptors are employed as solid state films in Xerographic machines (7). As a result, problems in charge separation in organic films and mechanisms of organic film degradation have also become active areas of commercial research organizations. Breakup of the exciton within the exposed organic film to produce separated electrons and holes has been found to occur in the bulk for some molecules and at the interface with the contact for others. The stability of such films is sufficient for commercial use, but only at the low irradiance used in Xerographic copying, which is about 1% of the level expected for solar photoconversion. Nevertheless, research into mechanisms of film degradation is needed.

Many advances have been made recently with electroluminescent devices based on polymers and evaporated devices composed of small molecules (8,9). The efficiency of these emissive materials depends on charge transfer at the metal/polymer contact and charge transport within the layers (10,11). The electron and hole injected at opposite contacts in the polymer devices are often designed to recombine at organic molecules pendant on the polymer chain. Solid state emissive systems assembled through evaporation, mostly involving aluminum tris(8-hydroxyquinoline) complexes, involve junctions between organic electron conductors and hole conductors. It is evident that charge recombination in these devices is the reverse of the problem of charge separation in organic molecular solar energy cells, and an understanding of these recombination processes has direct relevance to photoconversion systems. Similarly, the understanding of charge injection at the contacts, both organic/organic and metal organic, is as problematic in these emissive systems as it is in organic molecular solar cells.

A unique interface and contact between crystalline solid and nanocrystalline materials is found in the various forms of porous silicon that have been made (12,13). The photoelectrochemistry and of the nanocrystalline Si (14,15) can be modulated by the bias on the crystalline material, and the photoelectrochemistry has been found to influence the emissive characteristics of the nanocrystalline Si.

Challenges and Difficulties

Significant improvements can be made in the performance of these photoconductive systems under discussion. These improvements are to be found in both conceptual and pragmatic avenues of approach. Conceptually, they reside in the understanding of the sequence of events that follow photon absorption: exciton transport, charge transport, energy transfer, interfacial energetics, and electron transfer as a function of the interfacial energetics at an electrode or contact. Pragmatic material and systems work can establish the effect on the system photochemistry of reagent purity, material crystallinity, and thin film deposition techniques.

Much is known about these conceptual parameters in model semiconductor systems and in polycyclic aromatic molecular crystals; (16) there is a sound literature base on the fundamental controlling steps of charge separation and recombination, charge transport, and charge collection in these model arrangements. However, these steps have been less well characterized in the heterogeneous layered systems and devices described above. All of the characteristics are affected

by method of system preparation and layer deposition and by the nature of the materials and their immediate microenvironment.

On a practical level, there is a general lack of the supporting technologies which would enable improvement of the energy transduction in these systems. There is little knowledge about how ohmic contacts work in molecular systems, although some contacting schemes seem to work. This understanding is needed in these devices. The concept of "doping" is not well developed, either in theory or in practice. The purity requirements for the dyes are not clear. It is only known that the dyes used in the vapor-deposited systems retain impurities of 2% or worse and suffer in performance until these impurities are removed. Compared with the number of inorganic compounds that have been surveyed for photoelectrochemical studies, there have been relatively few organic dyes that have been examined with the requisite state of purity.

Meeting these Challenges

Meeting these challenges requires further studies in photochemistry in a number of areas. Some of these topics are device related, but many require studies at a very basic level.

One basic concern is the generation of charge carriers following photo-excitation. The mechanism of dissociation of the exciton needs to be determined so that it may be explained why some excitons dissociate at the interface and others in the bulk at defects. This behavior must be related to dye structure, molecular packing, and crystallinity. It should also be related to theories of charge transfer. Much is known about photoinduced charge generation in organic liquids and in crystalline polycyclic aromatic hydrocarbons. To what extent can this understanding be carried over to solids of low dielectric constant in the environment of these systems? Can these dynamic characteristics of the exciton be determined in representative model systems?

Charge transport is another area needing further inquiry. Differential transport of electrons and holes is well known in solid state organic electroluminescent devices and in organic photoreceptors for xerography. Yet the knowledge and experience in this domain have yet to be translated to organic solar cells. In molecular systems the charge carriers separated from an exciton move by a hopping mechanism which is severely inhibited by defects and impurities. Why a molecule or crystal enhances transport of one charge relative to the other should established? Is it determined by defects or by the intrinsic character of the charge transfer reaction?

When these carriers reach an interface, what type of contact is found? Both organic/organic and metal organic interfaces need to be studied. What is the relation between the energy diagram of the interface and the type of contact formed? Does the observed behavior correlate with theories of charge transfer? A theoretical understanding of these processes would enable a better cell modeling for comparison with real performance.

Crystallinity in these cells has been sought through the liquid crystal techniques and through slow vapor deposition (17,18). This molecular packing has a role, which should be quantified, in

determining electronic properties. Other self-assembly procedures for dyes in organic solar cells should be explored.

The requisite degree of crystallinity will have to be attained in large area fabrication. In going to larger areas, new procedures for low disorder deposition may be required, ones that leave few pinholes or other defects. Work with device fabrication has been limited to vapor deposition because spin-coated cells have yielded inferior results; it is the latter technique which is the more cost effective and a preferable approach to large scale device assembly. A spin-coated layer would benefit by self-assembly behavior in the molecules. Large area fabrication of organic assemblies must be explored to yield a device without pinholes and other defects.

It is necessary at one point to determine the degree of purity of the dye that is necessary to assemble efficient solar cells. The use of pure dyes in a cell are crucial in the extraction of accurate parameters necessary in the modeling of photoconversion systems.

In addition to these considerations on materials and the photochemical behavior of materials, there is a need for further development of new experimental techniques. Current-voltage data alone will enable only a limited understanding of these systems. In addition to standard optical techniques such as Raman, absorption, and emission spectroscopies, non-linear techniques should be amenable to the study of these systems. Second harmonic generation (SHG) and sum frequency generation (SFG) could be applied to probe interfacial fields. For the dynamic processes of charge relaxation in bulk and at the interface, ultra-fast probes could be utilized.

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PANEL A-2

SOLID STATE PHOTOCHEMISTRY

Subpanel A-2(a)

Design of Molecular Precursors for Electronic Materials

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Abstract

Recent achievements of synthetic chemistry in the field of electronic materials are presented in three categories; *viz*, precursor design for improved processing, new chemistry for selective growth, and new growth techniques. This is followed by a discussion of challenges and opportunities in two general areas designated as composition and structure, and growth and processing.

Preamble

The focus of this section is on fundamental projects having long term payoff. It targets the discovery and exploitation of basic research to enhance expansion into technology-driven arenas. We have chosen to address DOE-intensive areas currently suffering excellent physics and engineering at the hand of ill-understood chemistry. Some of these items are not perceived as "glamorous" for academic chemists driven by the ego boost of a once-a-decade *Science* article. It must be pointed out, however, that the research philosophy of the past five decades -- the hey-day of synthetic organic chemistry -- that has promulgated the US academic research enterprise, has roots firmly imbedded in targeted investigations -- specifically the necessity of providing a ready supply of pharmaceutical materials of obvious benefit to the public. Thus, this subpanel discounts the prevailing notion found today in many of the halls of academia that the only projects worthy of investigation are those classed as "curiosity-driven." The fresh ideas here will augment the long-supported fields of BES. This fundamental science -- focused on designed precursors -- is the basis of effective research employing resource utilization in targeted areas of significance.

Why This Research?

Synthetic chemistry is the Genesis of the entire electronic materials food chain. The point was stressed that tens to hundreds of millions of dollars of funding have been invested in selected electronic materials areas by DoE over the past one to two decades that even today do not have the demanded purity. We propose that such embryonic investigations of molecular precursors as outlined herein are mandated at this stage of the overall photovoltaic field. Furthermore, we assert that the rational design of such precursors is just over the horizon, and that substantial benefits from these explorations are anticipated to accrue to a diverse array of energy-related technologies encompassing a wide range of electronic materials.

What Knowledge Will Emerge From This Approach To This Problem?

See the outline presented in the following sections.

Why DOE?

Photovoltaics are a major component of the existent ER and EE portfolio; however, they lag in the commercial sector due a poor understanding of fundamental basic chemistry. We see a direct benefit to BES in this work. Most particularly, the key issues in PV appear to be coupled closely to the presently ill-understood role(s) of dopants in these materials. We propose that five to seven year term initially funded projects be implemented in a few select research groups having a successful track record in precursors for manufacturable electronic materials (e.g., Barron, Beachley, Buhro, Cowley, Gladfelter, Higa, Rees, and Wells).

Background

Fabrication of complex structures from simple molecular species is the cornerstone of much modern materials synthesis. Applications in high and medium technology rely on synthetic chemistry during one or more steps in the manufacturing process. Some of the chemistries have been developed to a high degree of sophistication, however, others still are in their infancy. Molecular precursors can be broadly defined as molecules whose reaction or decomposition, in isolation or in the presence of other compounds, leads to the formation of a solid state material. Conversion of a molecular precursors to a solid state material can occur from the vapor, liquid (solution), or solid phases. The method of conversion may be due to thermal, photochemical or plasma induced reactions. In the area of energy technology, especially with regard to photovoltaics, the synthesis of thin films of electronic materials is a clear application of molecular precursors. However, the active semiconducting layer is not the only area that precursor chemistry impacts. Conductors (both metal and non-metal) are required for contacts, while insulators (dielectrics) are required for isolation, passivation and optical coatings.

Recent Achievements of Synthetic Chemistry in the Field of Electronic Materials

The following represents an outline of some of the areas of electronic materials that synthetic chemistry has impacted recently, with a particular emphasis on those in the area of materials for photovoltaic devices.

Precursor Design for Improved Processing

The use of organometallic precursors for the thin film growth of semiconductor (and other) materials by CVD and related techniques requires precursors which must meet a series of chemical and processing requirements in addition to economic considerations (1). Synthetic chemistry has made significant advances in all of these areas. Examples are given below of some of the specific advances that have been made in recent years.

Improved Precursor Purity

The requirement of 99.9999% purity for alkyl indium compounds, in particular trimethyl indium ($InMe_3$), for the MOCVD growth of InP for specialized solar cells was met by the development of adduct purification methods.

Lower Toxicity Precursors

The extreme toxicity of arsine (AsH_3), used in the growth of GaAs led to the development of alternatives such as *tert*-butyl arsine ($^tBuAsH_2$).

Increased Volatility

Significant advances have been made to develop precursors with improved volatility required for CVD processing. Metallic copper is now routinely deposited using Cu(hfac)(trimethylvinylsilane), where hfac = hexafluoropentanedionato, which has a vapor pressure of 1 torr at room temperature.

Aerosol-Assisted CVD

While synthetic chemistry potentially is able to provide a nearly unlimited variation in molecular structure, there are limitations to volatility. In addition, there also are problems associated with precursors whose volatilization is accompanied by premature decomposition. However, films may be grown using alternative delivery systems, which, to some degree, circumvent these issues. Aerosol-assisted CVD allows for the transport of involatile precursors into the reaction chamber.

Selective Deposition

Precursors now exist that allow selective depositions of metals, in particular tungsten, aluminum, and copper (2), as well as of elemental (3) and compound semiconductors (4). In the case of compound semiconductors, the selective chemical reactions can be sensitive enough to grow only on a specific crystal face (5).

New Chemistry for Selective Growth

The ability to control structure, composition, and spatial arrangement are significant advantages to materials growth attained by the application of precursor chemistry.

Phase Growth Through Molecular Control

In principle, MOCVD offers a unique advantage over physical vapor deposition methods; the structure of the deposited film may be controlled by the structure of the precursor molecule. The first clear example of this effect is the growth of a metastable cubic phase of gallium sulfide (GaS) (6). The formation of this new phase of GaS may only be attained by the use of a cubane precursor, $[(R)GaS]_4$, and the retention of the Ga_4S_4 core throughout the growth process has been demonstrated. Thus, the growth of a previously unknown phase was a consequence of molecular control. The cubic-GaS has been shown to be the ideal passivation/dielectric coating for GaAs. The observation that previously undiscovered (metastable) solid state phases may be prepared by use of molecular precursors, having predesigned molecular motifs, offers the possibility that a range of materials may be prepared with a diversity of possible applications.

Nanoparticle Reaction Chemistries

The synthesis of semiconductor nanoparticles, such as metal oxides, metal halides, and metal chalcogenides is well known in colloidal chemistry. The first reports of the synthesis of II-VI colloidal nanocrystals with diameters less than about 10 nm that exhibited quantum size effects

occurred in the early 1980's (7). Semiconductor nanocrystals in the quantum size regime are also called quantum dots; they show large increases in band gap as the particle size decreases, as well enhanced photoredox chemistry compared to bulk semiconductors (8). Narrow size distributions (< 5%) of II-VI quantum dot colloids have been achieved using "Ostwald ripening" in coordinating solvents (9). III-V semiconductor nanocrystals and colloidal quantum dots have been synthesized since the late 1980's (10). Relatively narrow size distributions (< 10%) have been achieved with InP quantum dots, and high quantum yields for band-edge emission (> 60%) have been reported (11).

Preparation of Polytypes

The two polytypes of CDs, Greenockite and Hawleyite, each may be prepared from designed $Cd(SR)_2$ compounds. The mild thermal preparation of Hawleyite in 1995, permitted the isolation of highly pure, metastable material <1,000°C below its previous report (12).

New Growth Techniques

Along with new precursor systems, synthetic chemistry also may be central to the development of new growth methods. These new growth methods either allow for growth of new physical forms (*e.g.*, whiskers), improved film morphologies (*e.g.*, smoothness), or growth under unique process conditions (*e.g.*, lower temperature).

Low-temperature Solution Growth

The formation of crystalline semiconductor materials at or just above room temperature is desirable from a number of processing considerations. By the use of unique chemistries there have been several resent examples. Room temperature synthesis of polycrystalline $CuInS_2$ has been achieved through the reaction of $InMe_3$ with copper sulfide clusters, however, the applicability of the reaction is limited due to the formation of powders (13). Very recently, crystalline HgS has been prepared at *sub-ambient* temperatures through manipulation of selected precursors and reaction conditions (14). In contrast, whiskers of some 13-15 compound semiconductors have been prepared through a technique of solution-liquid-solid growth (15).

Aerosol Assisted Deposition of PV Materials Using Nanoparticle Precursors

The spray deposition of CdTe films from nanoparticle precursor colloids has been reported recently (16, 17). This method possesses several advantages over standard spray deposition, such as reduced processing temperatures and production of smoother, denser films.

Challenges and Opportunities

Following are areas of basic precursor research.

Composition and Structure

Phase and Composition Control

CVD of pristine aluminum films can be accomplished using triisobutylaluminum (18). Under similar conditions, trimethylaluminum produces a carbon-rich aluminum film exhibiting poor conductivity and optical properties. This is a striking example where a seemingly small change in the molecular structure of the precursor influences the composition of the solid state material. One goal in the area of molecular precursors involves the use of specific chemical reactions to control both the composition and phase of the product. Examples of controlling the crystalline phase by variation of the precursor structure are much less common (6) and such discoveries remain largely serendipitous. Establishment of principles governing growth of specific phases is needed, and to accomplish this more examples are needed. Titanium dioxide, for instance, commonly occurs in two crystalline phases, anatase and rutile. Can low temperature reactions producing nanocrystalline particles of TiO_2 having the rutile structure -- metastable below 700°C -- be developed? Can molecular precursors be devised to produce presently unknown phases of known solids, for instance an anatase-like phase of SnO_2 or a cubic form of GaN?

Dopant Atom Location and Concentration in Electronic Materials

The opportunity in site specific doping of electronic materials relates directly to one of the ubiquitous intellectual challenges of materials chemists, who strive to obtain rigorous three dimensional spatial control over atomic lattice placement. Two major successes in this field have occurred in the past five years. Rees has made ZnSe:N (19), a blue laser candidate, as well as GaAs:Er (20). Si:Er (Kimmerling) is the only presently proven method of obtaining light from an indirect band gap material. Significant current issues are in highly efficient alternate blue lasing materials, bright electroluminescent phosphors for full color flat panel displays, and long lived and inexpensive photovoltaics. Site specific doping should be a substantial BES initiative for improvements in CIS, CIGS, CDs, CdTe, $CdTe_{1-y}S_y$, $CdS_{1-x}Te_x$, a-Si:H, and a-Ge:H. The motivation here is a direct payoff of fundamental synthetic, structural and mechanistic explorations.

Applications of Quantum Dots

Quantum dots have potential applications for efficient, low-cost solid state and photochemical photovoltaic cells, and in novel optoelectronic devices. These applications frequently require the synthesis of monodispered, high-quality nanocrystals with completely passivated surfaces; this leads to high efficiencies for photoinduced charge separation, highly efficient photoluminescence, and optimum nonlinear optical properties. Novel quantum dot configurations can be fabricated in core-shell structures, sandwich structures, and as ordered 3-D arrays (3-D superlattices).

Interfacial Control

Electronic and compositional control over semiconductor surfaces and interfaces plays a decisive role in the usefulness of any semiconductor material. Applications include: chemical compatibility

of heterojunctions, and the electronic and chemical passivation of semiconductor surfaces to eliminate interfacial traps. Knowledge that must be gained to control interfaces includes an understanding of miscibility of heteromaterials and bond energetics. Research areas that must be addressed include: the rational formation of metastable phases and interfacial layers, as well as routes to new materials that meet the electronic compatibility issues that are key to passivation.

Growth and Processing

Mechanisms

One of the critical challenges in this area is to understand the mechanisms of reactions used to convert molecules to solid state materials. Ultimately we should seek the same molecular level understanding of these reactions that has been so incredibly valuable in advancing our knowledge -- and the predictability -- of homogeneous chemical reactions in organic and inorganic chemistry. In chemical vapor deposition, the interplay between gas phase and surface reactions must be understood. In situ methods should be incorporated into processes to establish the identity and concentrations of intermediate species. Surface science methods must be made realistic to conform to practical growth, in order to explore the reactivity patterns of more complex adsorbates including organometallic compounds. The identification of important reactions and the measurement of accurate kinetics, implicit in any thorough mechanistic study, will provide vital information for the development of meaningful growth rate models. This provides a direct bridge between the study of fundamental reaction mechanisms and the ability to design a suitable commercial deposition processes.

Alternative Deposition Strategies

Non-conventional Growth Techniques

Opportunities for improved growth and processing using alternative growth approaches include both new growth techniques as well as new delivery strategies for traditional deposition techniques. With respect to new growth techniques, the following two approaches should be considered: photochemically-initiated CVD, and spray deposition of polycrystalline materials using nanoparticle precursors. Photochemically-initiated CVD potentially permits film growth of targeted materials at reduced temperature and with better spatial resolution versus standard CVD -- if photon-induced precursor decomposition is present. Potential impact areas include growth of metal films on thermally-sensitive substrates,. The synthesis of new photosensitive CVD precursors presents a substantial research opportunity for this approach. Aerosol-assisted deposition of polycrystalline materials using nanoparticle precursors represents a growth technique that allows the development of smooth, dense thin films at reduced temperatures. This cost-effective approach has the possibility of being employed for the thin film growth of any polycrystalline electronic materials of interest; given the availability of a nanoparticle precursor colloid. The design of synthetic routes to nanoparticle colloids of materials that can be employed in PV and related electronic devices is therefore also of significant interest.

Alternative Delivery Techniques for Traditional Growth Modes

The final properties of a material should drive the essential cardinal explorations of the basic sustaining science. This effort often is form dependent, and particles, thin films and bulk materials each require somewhat different fabrication approaches. Often these decisions are interrelated to the stability of a desired substrate. This non-blue-sky area can be termed "new engineering for existing precursors" and may be contrasted with the alternate mode of retaining present deposition schemas and designing new precursors to shoe-horn into them. Included in this category are direct liquid injection (MKS) (21), solid source delivery (Hiskes, H-P) (22), and solution delivery (ATMI) (23). One touted advantage of these approaches is the short-term insertion into present-day processes. Although attention should be paid to this area, we have adopted the tone that a more beneficial long term payoff resides in the design of molecular precursors for electronic materials.

Nucleation Control

In CVD processes, the number density of nuclei initially formed on the surface of a substrate can play a critical role in determining the microstructure of the final film. Numerous methods have been empirically developed to control nucleation. For instance, one approach to the preparation of diamond films requires that the substrate be scratched with diamond powder to create nucleation sites before beginning the deposition (24). Chemical pretreatment of surfaces also has been successful. For example, pre-exposure of a substrate to $TiCl_4$ has been used to promote the formation of aluminum films in CVD processes at lower deposition temperatures and with improved optical reflectivity (18b). There are many fundamental questions that need to be addressed. An understanding of how the growth of particles depends on particle size is needed. When chemical pretreatments are used, what are the specific reactions that occur?

Process Control for Vapor Phase Manufacturing of Photovoltaic Materials

Manufacturing of a product related to photovoltaic energy production is of substantial economic and ecological importance to the United States. Implementation of intelligent processing strategies can influence dopant sub-lattice site residence, enhance feed reagent utilization, suppress co-product formation, and increase overall throughput to a competitive level. The implementation of *in-situ* diagnostics, with feedback-coupled control loops, will lead toward design of specific precursors that are not only composition, but also process, specific. We envision a predictive time where the engineer will prescribe a set of physical properties for the synthetic chemist (vapor pressure, thermal stability, atomic composition, etc.) and then receive not only the desired precursor in return, but also a recipe for the most beneficial manufacturing application of the specific composition.

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PANEL A-2

SOLID STATE PHOTOCHEMISTRY

Subpanel A-2(b)

Metastability in Hydrogenated Amorphous Silicon

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The Major Issues

What are the mechanisms of the photo-induced metastabilities in hydrogenated amorphous silicon and other thin film PV materials, and how can these photo-induced changes be reduced so as to improve device performance and long term reliability?

Present Status

All device quality amorphous silicon based materials exhibit degradation in electronic properties when exposed to sunlight. The photo-induced defects are associated with Si dangling bonds that are created by the recombination and/or trapping of photogenerated carriers. The defects are metastable and can be annealed out at temperatures of about 150 to 200 degrees Centigrade. The density of metastable defects is larger in films that are contaminated with $> 10^{19}$ per cubic cm of impurities such as oxygen, carbon and nitrogen. However, recent experimental results indicate that some metastable defects are still present in films with very low impurity concentrations. The photo-induced defects typically saturate after 100 to 1000 hours of exposure to one sun illumination depending on the deposition conditions. There is also experimental evidence that photo-induced structural changes are occurring in the amorphous silicon based materials and that hydrogen may be playing an important role in both the photo-induced structural changes and in the creation of metastable defects.

The stability of these materials can be improved by growing the films by plasma-enhanced CVD in an atmosphere of silane diluted in hydrogen as compared to an atmosphere of pure silane (hydrogen dilution of the discharge atmosphere appears to improve the microstructure of the films). The stability of amorphous silicon solar cells is currently optimized by utilizing relatively thin active layers (about 200-300 nm) so that most of the photogenerated carriers are swept out of the active layer by the strong internal fields before they can create metastable defects through recombination or trapping.

Performance Barriers

Present commercial single-junction amorphous silicon solar cells typically degrade about 20-30% before stabilizing, while multijunction cells degrade by about 15 to 20%, thereby yielding stabilized conversion efficiencies of about 10% in optimized devices. However, if the amorphous silicon based materials could be completely stabilized through the elimination of photo-induced defect formation and photo-inducted structural changes, then the conversion efficiency of amorphous silicon solar cells would increase from ~ 10% to about 15% since the device could be made thicker, and absorb solar radiation more effectively. The Electric Power Research Institute (EPRI) estimates that more than 1 gigawatt of grid-connected electrical power could be supplied by PV over the next decade if a low-cost PV module could be developed with a conversion efficiency of about 15%. Moreover, even larger markets would exist overseas for both grid-connected and remote power applications in both developed and developing nations. Thus, understanding and eliminating the photo-induced degradation in amorphous silicon based materials could give rise to a multi-billion dollar business that could bring low-cost, non-polluting power to people everywhere.

Challenges/Opportunities

Six general areas that require further investigation have been identified by the panel members:

(1) The role of hydrogen in amorphous silicon based materials.

Hydrogen plays a dual role: I) acting a dangling bond terminator in as-deposited materials, but ii) it also appears to be involved in the microscopic processes that promote photo-induced structural changes and defect generation.

(2) The microstructure of amorphous silicon based materials.

The amorphous silicon based materials used in PV technologies are alloys of silicon, hydrogen, and in addition, alloy additives such as carbon and germanium that are used to tune optical absorption properties to match the solar spectrum. The microstructure of these materials, including voids, clustering, etc., plays a role in determining their electronic properties and also influences the formation of defects and defect precursors for photo-induced effects.

(3) The properties of amorphous and microcrystalline alloys.

The photoelectronic properties of thin film amorphous and microcrystalline silicon based alloys are functions of their alloy chemistry and the microstructure, and must be investigated to improve device performance and stability.

(4) The role of interfaces in determining the stability of devices.

PV devices are multilayer structures comprised of photo-active regions (in which solar radiation is absorbed and converted into electron-hole pairs), as well as high conductivity doped regions (that are required for carrier extraction and to establish an internal electric field). The transport and recombination properties of interfacial regions therefore play important roles in device performance, and can be a factor in photo-induced defect generation and photo-induced structural changes.

(5) The kinetics of defect creation and annealing.

The rate of defect generation and annealing under operating conditions determines the steady-state photo-response and the stabilized conversion efficiency, and hence is critical in determining overall PV performance.

(6) The role of charge-state dependent effects related to Fermi level shifts and defect relaxation.

Photo-induced metastability is strongly influenced by Fermi level shifts, single charge injection and trapping of charge. These metastable effects may be similar to defect configurational relaxations caused by charge trapping. Also, the Fermi level variation across the photo-active light absorbing regions of a solar cell causes gradients in both defect type and density that influence the stability of cells. Understanding these issues may lead to new strategies for amelioration of the light-induced defect problem.

Specific areas of research that should be investigated include:

- a careful examination of the material properties under extreme conditions such as very short laser pulses, high light intensities, low temperatures, high electric fields, etc. These studies will provide information on the photo-induced defect generation and photo-induced structural change mechanisms, including the kinetics of annealing.

- growth and characterization of amorphous silicon based materials with relatively low hydrogen concentrations. These studies will provide a data base for understanding the role of hydrogen, both as a defect passivator in the as-deposited films, and as a defect precursor material in photo-induced degradation processes.

- materials made with passivants or bond terminators other than hydrogen. These studies will be useful in determining if combinations of hydrogen and other elements can produce alloys

which can be tailored to provide absorption of solar energy, to provide efficient transport and separation of photo-generated electron-hole pairs, and at the same time to provide more resistance to photo-induced degradation effects than the materials systems currently employed in devices.

- an investigation of the interaction of light with polycrystalline and microcrystalline silicon and the role of hydrogen in these materials. These materials can be produced by thin film deposition processes; the role of hydrogen in defect passivation and photo-induced degradation processes must be studied to evaluate their potential for use as materials alternatives in PV devices.

- determination of the influence of light on defects, dopants, impurities and hydrogen in these materials. These studies will provide a basis for separating the roles of structural defects (e.g., voids), dopant atoms, impurities (e.g., oxygen and nitrogen), and hydrogen in photo-induced defect generation and photo-induced structural change mechanisms.

- determination of the relationship of light-enhanced hydrogen motion to photo-induced metastability and photo-induced structural changes. These studies will determine what role hydrogen atom or ion motion plays in photo-induced metastability and photo-induced structural changes, and thereby provide insights into photo- and thermal annealing processes as well.

- detailed studies of the local environmental changes caused by light using techniques such as NMR, x-ray scattering, neutron scattering, positron annihilation, etc. These studies will provide microscopic information on changes in local bonding and structure that take place during photo-induced metastability, photo-induced structural changes, and thermal and photo-induced annealing processes.

- an investigation of photo-induced metastability and photo-induced structural changes in hydrogenated amorphous germanium. Comparisons between photo-induced metastability, photo-induced structural changes, and thermal and photo-induced annealing processes in hydrogenated amorphous silicon and germanium will be useful in providing increased knowledge of microscopic processes, and will allow us to more accurately estimate theoretical and practical limits to device performance.

- the effect of alloying on the photochemistry in amorphous silicon based materials. Alternative alloy materials, e.g., hydrogenated amorphous silicon nitrogen alloys should be investigated to determine how differences in local bonding chemistry and coordination affect photo-induced metastability, photo-induced structural changes, and thermal and photo-induced annealing processes.

- the influence of voids, clusters, strain on photo-induced effects. These studies will determine relationships between thin film microstructure and photo-induced properties, and coupled

with studies of different alloy and dopant atoms will provide important insights into the inter-relationships between microstructure and chemical bonding.

- developing a better understanding of the energy dissipation mechanisms following photo-excitation of amorphous materials. These studies will provide insights in the way energy is dissipated in photo-excitation and recombination processes, and coupled with studies of alloys, dopants, impurities and microstructure will provide guidelines for optimizing device performance.

- more careful studies of irreversible photo-induced effects in amorphous materials. In order to optimize long-term device performance, it is necessary to determine the time scales for reversible and irreversible photo-induced effects in the photo-active intrinsic and the doped layers of PV device structures.

- a better understanding of the photochemistry of defect generation and photo-structural changes at interfaces. It is important to separate interface and bulk layer photochemistry in order to optimize carrier collection and minimize defect generation.

- increased theoretical studies of local bonding , defect-generation and annealing processes in amorphous, microcrystalline and polycrystalline silicon based materials. A better theoretical understanding of the electronic and topological structures of these materials may be obtained using such powerful tools as QM molecular dynamic simulations. Theoretical studies will help in the interpretation of experimental results in the areas identified above and will provide guidelines for the development of new materials and novel cell structures.

General Recommendations

In general, it is very important to develop a better understanding of the interaction of light with amorphous, microcrystalline and polycrystalline materials, and especially to understand the mechanisms associated with photo-induced metastability and photo-induced structural changes in hydrogenated amorphous silicon and related materials. Progress in this area would likely be accelerated if a center were established where unconventional deposition techniques (e.g., those not employed in the present day manufacturing approaches such as photo-CVD, hot wire CVD and remote PECVD) could be tested in conjunction with conventional PECVD methods of growing amorphous silicon based materials. Such a center would allow one to insert layers of new materials into device structures without contamination of the interfaces. For example, p-I-n solar cells could be fabricated by using unconventional techniques to deposit photo-active amorphous or microcrystalline I-layer materials in conjunction with doped n+ and p+ regions deposited by conventional glow discharge processes. Moreover, the equipment could be configured with in-situ diagnostics to characterize the properties of the surfaces, interfaces and bulk materials.

This approach has provided useful information in other multilayer devices including gate stacks, comprised of crystalline silicon substrates, nitrided dielectrics, and doped polycrystalline layers in

field effect transistors. The development of such a center would provide timely and accurate evaluation of new material packages for device structures, and as well as insights into photo-induced metastability, photo-induced structural changes, and thermal and photo-induced annealing processes. It will also provide a cost effective way of evaluated new materials without requiring each of the contributing groups to duplicate many of the cost and technology intensive steps of PV device fabrication.

Summary

Past support for fundamental research into the properties of amorphous materials has led to the development of products such as photocopiers, thin-film transistors for flat panel displays, thin film solar cells, photodetectors for imaging devices, etc. DOE support for research into photo-induced effects in amorphous materials may lead to a multi-billion dollar PV business that could impact the quality of life worldwide.

PANEL A-2

SOLID STATE PHOTOCHEMISTRY

Subpanel A-2(c)

Challenges and Opportunities in Photochemistry

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Abstract

In contrast with the prior two subsections, the topics in solid state photochemistry range from photo(thermal)-induced degradation to synthesizing new compounds with desirable functions or properties. We will therefore discuss the importance of each relative to existing technological barriers, recent progress, potential applications, and the advantages expected from new information from basic science, especially, as it relates to the DOE mission.

Prepare or Investigate Photostable (Polymeric) Materials and Glasses

Importance. Multilayer devices, as shown in Fig. A2C1, used for collecting, absorbing, or redirecting solar radiation must perform their function for 20 to 30 years or more (1,2). The purposes of the layered structures include providing a support substrate, protecting the active material from weathering degradation, and providing stability for the device from hail, wind, dust, rain, etc. If photothermal degradation occurs in any material or at any interface, the device properties may be compromised, shortening the service lifetime and increasing the life-cycle cost.

Background. The materials currently in use are ethylene vinyl acetate (EVA) as a pottant in PV modules (3), polymethylmethacrylate for silvered solar mirrors (4), and several polymers as the ion conducting layer in electrochromic devices (5), all degrade photothermally in the bulk polymer or at the polymer/silver interface. Organic polymers have been used in the past because they are inexpensive, serve numerous functions (6), and are easy to use in industrial fabrication processes. The present technology depends on using UV absorbers, UV stabilizers, and thermal antioxidants as additives in an attempt to stabilize a photodegradable polymer; the weaknesses of the "stabilization" approach have been reported for EVA (3). Likewise, solar transmitting glasses must be inexpensive, stable in weathering environments, and be easy to use in industrial processes.
A number of opportunities that are part of the major challenge and the technological barrier circumvented are as follows: 1) identify and use monomers with potential for making photostable polymeric coatings/encapsulants (3) with the desired technological properties (7); 2) identify the rate controlling photodegradation mechanisms in weathering environments, which are critical for comparing with those under accelerated UV, temperature (T), and relative humidity (RH) conditions; 3) synthesize polymeric materials with low permeability to gases/vapors that destructively react with the active materials (e.g., Ag, Si, $CuInSe_2$, CdTe, a-SiH) or their surfaces; 4) synthesize stable low-energy surfaces that will not be subject to soiling and thus maintain optical transmittance for solar radiation; 5) establish the wavelength dependence and environmental stability of amorphous materials that prematurely compromise their performance function; 6) understand structural changes in materials exposed to simulated (accelerated) and natural weathering environments that can result in premature loss of one or more important functions of the material; 7) establish the compositional/structural limits of stable less-dense, porous and organic-inorganic glasses that could eliminate the elastomeric needs for organic polymers; 8) identify degradation mechanisms at interfaces (e.g., polymer/glass, polymer/metal oxide, glass/metal oxide interfaces), that result from weathering environments; 9) establish solar intensities (e.g., 100, 500, or 1000 suns) that are allowable before (a) photothermal degradation mechanisms are altered (e.g., in polymers) or (b) before the onset of photodegradation occurs (e.g., in expensive but efficient materials such as GaAs and InP used in concentrator PV applications). The information in 9a is crucial for scaling factors between accelerated testing and real time testing conditions an in 9b for determining the upper limits for concentrators that cap the cost reductions achievable with concentrating systems.

Successful solutions of issues 1) through 9) all address in some way the life cycle cost or service lifetime of multilayer devices used in solar energy conversion systems. The impact of any solution will only be useful if the investigations begin with the idea of being able to transfer the synthesis or

process to an economically viable industrial scale or the knowledge and information to mitigate causes of performance losses in otherwise technologically successful materials, components, or devices. Any of the above research issues have potential for improving the performance or extending the service lifetime of existing energy efficiency and renewable energy (EERE) technologies that are (or soon will be) economically viable for producing power from solar radiation (e.g., solar mirrors and PV modules) or conserving the energy now needed for building applications (e.g., electrochromic windows).

To Understand the Photochemistry of New Lithographic Materials

Over the last 35 years enormous achievements of scale in photoresists have resulted in microelectronic devices of ever increasing capacity (8-11). Accompanying the development of new semiconductor materials for solar and electronic applications, a pervasive challenge will be for alternative lithographies for surface patterning that do not chemically change or in other ways alter underlying semiconductor properties during photoprocessing or development. New systems are needed that share the resolution, contrast, and speed of current commercial systems but can be patterned photochemically at multiple wavelengths and developed under different conditions. For example, commercial photoresists, developed mainly for silicon, are often less useful with new semiconductor materials. One or more of the processes required in forming the resist pattern irreversibly destroys the characteristics of the supporting semiconductor. Applications for new resists include Ga/As that needs to be etched for cleaning, island isolation, and the revelation of specific crystallographic planes, and CdTe where alternative development methods may hold numerous advantages. These, and others, are critical for many DOE applications.

Understand Electron Transfer in Solids at the Molecular Level

Understanding electron transfer at a molecular level in liquids has been greatly aided by better methods for observing reaction intermediates such as transient spectroscopy. Understanding electron transfer at a molecular level in solids is much more difficult, and a significant gap exists between what occurs in electron transfer and by means of which a device operates, and the molecular chemistry by which the required electronic changes take place. Research is necessary on the molecular properties of charge transfer donors and acceptors gathered as rationally synthesized assemblies. Studying the photochemical and photophysical changes that occur in these assemblies and developing new analytical methodologies to follow electronic changes in these assemblies will lead to increased understanding for the purpose of rationally changing such processes in future solid state devices. Since electronic changes in solids pervade current DOE interests, there studies are of high significance.

Synthesis of Organized Hierarchical Ordered Nanostructures Tailored to Perform Specific Functions ("Modular Chemistry")

In the course of the last few decades, chemists have greatly improved their ability to synthesize most organic and many inorganic molecular structures on demand. It is now possible to design a molecule

of prescribed dimensions, with functional groups in preselected locations with preselected orientation. Enough is known about the properties of functional groups to impart a desired set of properties such as light absorption and emission, electron donation or acceptance, polarity, volatility, etc. and to tune them by trial and error. An example of molecules designed to perform a specific function are those that develop a positive charge on one end and a negative one at the other in response to irradiation.

The perception of mastery rapidly fades at the next level of complexity, which is necessary if optimal use is to be made of these molecular modules. This is the production of organized structures built from the individual molecular modules (12), either by ordinary strong bonds (in which case the superstructure is a single macromolecule), or by weak intermolecular interactions (supramolecular assembly). The need for such secondary structure rapidly becomes apparent when one considers how the performance of each individual molecule is to interface with the outside macroscopic world. In the above example, the photoinduced charge separation in individual molecules is useless if these merely float in an isotropic solution.

An analogy could be drawn to biology: we may now know now to obtain a series of bottles, each containing one of the compounds that occur in a cell, but we do not know how to organize molecules contained in the bottles into a living cell, let alone how to organize such cells into an organism. Enough progress has been made in recent years in the direction of molecular organization that the time is probably ripe for a major research initiative towards developing a solid scientific basis for manufacturing molecular and assembling modules. This would greatly benefit photochemistry. For instance, if the molecules mentioned above could be assembled and oriented properly, a macroscopic charge separation would result upon irradiation. However, the impact of the desired developments would reach far beyond the discipline of photochemistry. For instance, it would be possible to engineer luminescent charge recombination layers that work at low voltage, optimized light frequency doubling plastic waveguides, and numerous other devices.

So far, progress has been primarily in three directions: (i) crystal structure engineering, (ii) synthesis on surfaces, and (iii) molecular recognition ("supramolecular chemistry"). The design of crystals for non-linear optics and the design of microporous crystals are perhaps the best known examples of the first category. Although periodicity in three dimensions greatly limits the scope of what can be achieved with ordinary crystals, for many purposes this type of superstructure control will be adequate. The use of surfaces permits an additional degree of control since now, perfect periodicity is present in only two dimensions, and structure in the direction perpendicular to the surface can in principle be controlled at will. Photolithographic techniques can be used to provide aperiodic structures in the first two dimensions as well, albeit at present not on molecular scale. Some examples of this type of work are the use of self-assembled and Langmuir-Blodgett monolayers and multilayers, the anchoring of polymer chains on surfaces, and the nucleation of crystal growth on surfaces. Molecular recognition, or "supramolecular chemistry," impacts both categories (i) and (ii). An improved understanding of the ways in which weak intermolecular forces cause molecules to assemble will aid both the attempts to engineer crystals and attempts to assemble molecules on surfaces.

The science of modular chemistry is presently in it infancy. Our limited ability to produce superstructures from molecular modules represents a serious barrier in the way of a full utilization of our ability to synthesize nearly arbitrarily structured molecular modules.

The type of research activity needed to overcome the barrier is multidisciplinary. It is likely that decisive progress will result from the use of surfaces for the anchoring of the superstructures. We need to know much more about the molecular nature of surfaces and about chemical reactions that occur on surfaces. We need investigators capable of synthesizing the right types of molecular modules as well as investigators capable of performing in-situ analysis of self-assembly reactions. Above all, we need imaginative new ideas about how to proceed. This is an archtypical high-risk high-payoff area of basic research.

Since many of the opportunities for the ultimate practical utilization of the fundamental advances that we feel ought to be pursued impact either energy conversion (e.g., photoinduced charge separation) or energy consumption (e.g., efficient electroluminescence), the Department of Energy is a logical beneficiary from research in modular chemistry.

Use Near Infrared Sources for Photochemical Changes

Electronic changes caused by the absorption of light and leading to chemical reactions include, among others, homolytic and heterolytic bond dissociation processes, and single electron oxidation/reduction reactions. Bond dissociation processes generally require higher energies than photooxidation/reduction reactions, with the latter benefiting from both the energy of the excited state and the electrochemical potentials of the donor and acceptor (13).

Cheap, compact, low power lasers emitting red and infrared light have existed for a number of years, yet because these are long wavelength sources, few molecular pairs can be induced to undergo chemical change by absorption of radiation from them. A significant opportunity exists to synthesize, construct assemblies, and study the chemical changes caused in molecules that undergo electronic transitions upon the absorption of radiation from 650 to 1000 nm. DOE has many potential interests in this research, from the construction of more photostable devices and assemblies to cheap, high resolution methods for lithographic absorbing systems such as black inks.

Identify Potentially Useful Photoinduced Charge Separation in Semiconducting Metal Oxides

In addition to detoxification or waste degradation, semiconductor-mediated photocatalysis has also been investigated for its potential application in a range of organic functional group transformations (14). These reactions include oxidation, reduction, isomerization, condensation, and polymerization (15). The potential applications of these reactions are in the area of environmentally benign chemical processes by using renewable (solar) energy to replace problematic (toxic or hazardous) chemical reagents such as strong oxidizing or reducing agents. The key barriers in this area include

the identification of significantly important chemical processes that can be conducted using semiconductor-mediated photocatalysis, and are economically comparable or superior to the conventional chemical process. Some exemplary opportunities in this area are:

1) Synthesis of potentially useful organic compounds. In addition to the routine requirement of high product yield (chemical and quantum), high selectivity, and low by-product yield, the synthesis should integrate the use of both oxidation and reduction characteristics of the photocatalysis. This may be accomplished either by forming the final product through the use of both electrons and electron-holes, or obtaining valuable products(s) from sacrificial electron donors or acceptors. The success of these types of processes should also be accompanied with a fundamental understanding of the reaction mechanism and influential factors, such as surface properties, surface/reactant/product interactions, and solvent involvement. Successful investigations of these types should also be coupled with the development or adaptation of a highly efficient photocatalytic reactor. The configuration of the semiconductor particles is preferably immobilized. The separation of the desired product(s) should also be addressed.

2) Metal oxide particles often need to be encapsulated (e.g., coated with organic polymer) for processing or protective purposes. The stability of these coatings (including their photostability) will have a direct impact on the economics and usefulness of these particles. The current practice is to use redox reagents or radical initiators for the polymerization process. The residues of these reagents may introduce undesirable physical or chemical properties, such as photoinstability. It has been demonstrated that photoinduced charge separation on some (semiconducting) metal oxides can induce polymerization (16). However, the application of this study to the polymer coating has not been explored. The success of research in this area will require a better understanding of the initiation mechanism(s), the requirement of the metal oxides, monomer, and environment. The targeted polymer coating should be mechanically as well as photochemically stable. The adhesion to the particle surface should be better than or comparable with those made with conventional methods. The photoinduced charge separation in these polymer-coated metal oxides may also induce the degradation of the polymer on the surface. The degradation mechanism and remedification of this type of degradation should also be addressed.

3) Actinometric or dosimetric measurements are needed for all applications in semiconductor-mediated photocatalysis. The current practice is the use of a photoelectrical or photochemical system. The disadvantage of these methods is the significant difference between the dosimeter (actinometer) and the semiconductor particles. Therefore, careful spectral corrections must be made for these methods. It has been demonstrated that photoinduced charge separation on semiconductor particles may lead to the trapping of conduction band electrons or valence band holes (17). The extent of the trapping can be correlated to the photon flux (18). Before such a system can be used in a photocatalytic process, some fundamental issues need to be addressed. These barriers include the correlation between the physical properties of the semiconductor particles and the trapping efficiency, the correlation between the trapping efficiency and the physical and chemical properties of the matrix material, the photostability of the particles and the matrix, etc. The success of this research requires an integration of the knowledge in particle synthesis, photoinduced charge

separation, electron-hole trapping, and matrix selection. The targeted dosimeter should possess the desired dynamic range for photon flux, flexibility to change the range, reproducibility, consistency, and reusability. For some applications, the system can be configured into a solid matrix.

Control Through Molecular Design the Excited State Properties for Optimizing the Desired Function(s) in Solid State Systems

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PANEL B-1

PHOTOCHEMICAL REDUCTION OF CO_2 TO FUELS AND CHEMICALS

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Abstract

Photochemical reduction of CO_2 represents a potentially useful approach to developing a sustainable source of carbon-based chemicals, fuels, and materials. In this report the present status of photochemical CO_2 reduction is assessed, areas that need to be better understood for advancement are identified, and approaches to overcoming barriers are suggested. Because of the interdisciplinary nature of this field, assessments of three closely interrelated areas are given including integrated photochemical systems for catalytic CO_2 reduction, thermal catalytic CO_2 reactions, and electrochemical CO_2 reduction. The report concludes with a summary and assessment of potential impacts of this area on chemical and energy technologies.

Introduction

Biological photosynthesis, the reduction of CO_2 using energy derived from sunlight, is the ultimate source of all of the fossil fuels and the majority of chemicals used today. Man's use of these materials far exceeds the rate at which they are being replaced by natural processes, and it is prudent that we seek other approaches to obtaining carbon-based materials that will be needed in the future. As a result of the combustion of fossil fuels the atmospheric concentration of CO_2 is increasing, and this has led to the general scientific belief that a significant warming of the earth will occur in the next 50 years. Processes which use CO_2 as a starting material have the potential for allowing the continued use of carbon-based materials without contributing to net CO_2 production.

The conversion of CO_2 poses many scientific challenges owing to its great stability and chemical inertness. The former leads to the necessity of energy input for the desired transformations. The latter generates the need for catalysts capable of binding, activating and transforming CO_2 to the desired products. The energy required for CO_2 reduction to fuels and chemicals may be provided by any of the following: 1) the absorption of light; 2) electrochemical addition of electrons; and 3) use of an energetic reductant such as hydrogen. In the context of photochemical reduction of CO_2, the first of these is clearly most desirable, but key aspects of strategies 2) and 3) relate to program objectives and merit further investigation as well. The following report outlines these different approaches, their current status, problems to be overcome, and some of the fundamental scientific questions to be answered for technology development.

Important considerations common to the three general strategies for reducing CO_2 relate to the kinetics and mechanism of catalysis (i.e., the binding, activation and transformation of CO_2), the energetics of individual reaction steps and the thermodynamics of the overall transformations of interest. Structure-reactivity correlations provide important means by which to understand and predict catalyst effectiveness and selectivity. Additionally, the research requires the synthesis of new catalytically active complexes and specifically modified systems to probe reactions mechanistically.

Photochemical Reduction of CO_2

The use of light to effect reduction of CO_2 may be accomplished in one of several ways. The first involves a system for artificial photosynthesis in which light absorption leads to electron-hole creation followed by electron transfer to yield charge separation, collection of reducing and oxidizing equivalents at dark reaction centers and catalysis of the appropriate redox reactions including CO_2 reduction. The second is related to the first but leads to generation of a reduced species, notably H_2, that can be used to reduce CO_2 subsequently. The generation of H_2 by water splitting using photovoltaics results in a similar situation with regard to CO_2 reduction. Since the conversion of CO_2 to other chemical entities in this context is strictly dark reaction chemistry, challenges related to this approach are discussed in the section on thermal CO_2 reduction. A third approach involves the reduction of CO_2 by direct photochemical reaction of metal-CO_2 complexes, while a fourth relies on metal complex chromophores that upon excitation show reactivity with CO_2. For each of the last

two approaches, the metal complex must possess interesting and unusual excited states that will promote the desired activation and transformation of the CO_2 substrate.

Coupling of Photo-induced Charge Transfer to CO_2 Reduction

The transduction of light energy to chemical energy via dark reactions at catalyst centers in a homogeneous or micro-heterogeneous system provides the basis for artificial photosynthesis. Key elements of such an artificial photosynthetic system are a chromophore and photoreaction center that effects electron-hole creation and separation, a molecular design that allows vectorial electron and hole transfer, and appropriate spatially-separated catalytic (dark reaction) sites. Recent work has focused on developing molecular excited states capable of charge separation and rapid electron transfer to external reagents. This area is in need of continuing development with respect to understanding the chemical and physical properties of the chromophore's excited states and the catalytic apparatus that will allow efficient reduction of CO_2. Previous studies have concentrated on homogeneous and micro-heterogeneous systems based mainly on transition-metal chromophores of d^6 ions such as Ru(II) and Re(I). New chromophores with strong absorption in the 400-800 nm region of the spectrum that will allow capture of solar energy efficiently and long-lived excited-states that will facilitate the electron transfer chemistry needed to promote the desired redox reactions are in need of further development and characterization. Additionally, the development of supramolecular assemblies that facilitate the sequence of steps required in photosynthesis including vectorial electron transfer and charge accumulation represents an important research objective.

A number of photocatalytic and photosynthetic systems have been examined that show promise in the photoreduction of CO_2 to CO, formate, or in rare instances, to methanol, methane and oxalate. The dark or possibly photo-catalyzed CO_2 reduction takes place after the initial light-induced charge separation in these systems. In many of these, the production of H_2 is an accompanying reaction channel. Control over the reaction channels to obtain product specificity is a desirable goal, as for example by changes in catalyst structure, chromophore excited states and energetics, and reaction medium. Mechanistic and kinetic studies are of great importance in determining the course of these reactions. The use of time-resolved spectroscopies (absorption, emission, IR, etc.) on intermediates will help resolve issues concerning the evolution of the catalytic process. Specifically, it is crucial to obtain insight into the identification of photo-induced charge separated species, the reactivity of the intermediates with CO_2 or H^+, the bonding nature of possible intermediates such as M-CO_2, M-H, M-OCOH, M-COOH, etc., the electrochemical potentials of the intermediates, and the fate of suspected poisoning reactions.

In this context, synthetic and mechanistic studies of bifunctional complexes may lead to specificity of product formation by encouraging self coupling of bound CO_2. Another possible reaction channel might involve the photoproduction of reactive species such as hydrides for subsequent reaction of CO_2. For all of the photosynthetic systems developed, mechanistic understanding can serve to improve quantum yields and turnover numbers for CO_2 conversion. Also by manipulation of relative barriers in competing reaction channels, it will be possible to influence product selectivity and lead

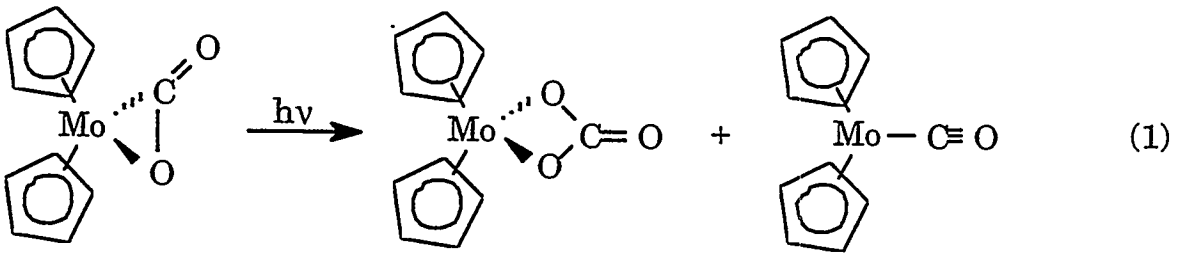
for example to desirable product mixtures such as synthesis gas (CO and H_2) from which methanol can be produced.

An alternative approach to charge accumulation is to generate two or more reducing equivalents not on the photo-reaction center or the dark catalyst, but as relatively stable chemical intermediates. These intermediates, formally analogous to NADH in PS I, must be able to transfer electrons or other reducing equivalents to the CO_2 reduction catalysts to carry out the desired multi-electron reductions.

Direct Photochemical Reduction of CO_2

Direct photochemical reduction of CO_2 is a process in which light and carbon dioxide are converted directly to a desired product without an intervening electron transfer sequence or generation of chemical reductant. One approach in this regard is the generation of an excited state chromophore that is capable of reducing CO_2 directly. This approach leads to the formation of CO_2^- which is a highly energetic species. While most chromophores are incapable of delivering the reducing power necessary to generate CO_2^-, there are examples in which this has been used in conjunction with subsequent addition to organic substrates in a light-driven carboxylation reaction.

Another means of direct photochemical reduction of CO_2 is via the excitation of M-CO_2 complexes such as $Cp_2Mo(CO_2)$. A reaction based on this complex is shown in eq. 1. Photoreaction of M-CO_2 complexes may lead to cleavage of a C-O bond of carbon dioxide and formation of either free or bound CO with transfer of the cleaved oxygen to either a metal center or another ligand. Studies on eq. 1 point to the possible involvement of M-CO_2-based excited states. Preparation of new complexes that contain lowest-lying MLCT (to CO_2) excited states or LMCT systems where an ancillary CO_2 ligand can be activated would serve to broaden the range of direct CO_2 photochemical reduction. Spectroscopic, electrochemical, and molecular orbital studies should be done in order to help characterize the electronic structures of M-CO_2 systems and identify new complexes for possible photochemical study. Understanding the electronic structure of these complexes may also lead to new reaction channels including C-C and C-H bond formation.



(1)

A relatively unexplored approach to direct photochemical reduction of CO_2 is the reaction of CO_2 with long-lived excited states that are capable of reaction chemistry beyond electron transfer. For example, complexes containing metal-hydride or metal-alkyl bonds may be induced to insert CO_2 upon excitation, leading for example to the generation of metal formate or metal carboxylate complexes. These reactions result in a formal two-electron reduction of the CO_2 moiety, but they must be extended to achieve catalysis. Studies should be conducted to elucidate the nature of excited states that are highly nucleophilic and reactive with CO_2. Understanding the mechanism of these light-driven reactions will be important to rational development of CO_2 reduction based on these systems.

A key problem in achieving light driven reduction of CO_2 is the fact that desired reductions correspond to even electron transformations and photochemical processes are single electron events. An approach to CO_2 photoreduction that does not depend on accumulation of charge in a dark reaction center represents an important research objective. Possible approaches include the use of metal-metal bonded systems and complexes that undergo disproportionation upon excitation yielding a net two-electron reduced site. Yet another approach to this problem may involve excitation of an intermediate generated photochemically or electrochemically to yield a species capable of transferring two electrons to a CO_2 substrate.

Thermal Catalytic Reactions

Understanding the thermal catalytic reactions of CO_2 is essential to the development of efficient and selective photochemical systems. Although dark reactions such as bond formation and bond cleavage reactions are slower than photoexcitaion of photocatalysts and electron-transfer steps, thermal reactions can be used to tailor photochemical systems to give a broad range of products by rational coupling of photochemical and dark reactions. In addressing thermal catalytic conversions of CO_2, the processes may be broadly categorized as: 1) hydrogenations; 2) carboxylations, and 3) redox (O-transfer) processes. Here we discuss selected challenges and new opportunities in these areas.

CO_2 Hydrogenations: Present Status and Challenges

Transition metal-catalyzed reactions, both homogeneous and heterogeneous, play a central role in the chemical and petrochemical industries. As an abundant and renewable carbon source, CO_2 is relatively unused for incorporation into bulk or commodity chemicals or for the production of fuels. The latter requires an energetic reductant which is most notably hydrogen. Possible sources of H_2 include: 1) steam reforming of natural gas; 2) the production of water gas from coal and steam at high temperature followed by the water gas shift reaction; 3) the Carnol process, which involves methane decomposition to C and H_2; and 4) the electrolysis of water. Only the electrolysis of water driven photochemically or through the use of photovoltaics represents a means of hydrogen production using a renewable energy source (This research topic was discussed in a concurrent panel. It is recognized that there are many areas of overlap, and that hydrogen production and CO_2

reduction represent complementary technologies.), whereas the principal method of producing hydrogen today is the steam reforming of natural gas.

Two examples of catalytic hydrogenation reactions utilizing CO_2 as a substrate are known which afford useful products. First, heterogeneous catalysts (e.g. Zn/Cu oxides) are effective for the hydrogenation of CO_2 to methanol under moderate conditions (eq. 2).

$$CO_2 + 3\,H_2 \longrightarrow H + H_2O \qquad (2)$$

More recently, active homogeneous Rh and Ru catalysts have been found which induce hydrogenation of CO_2 to formate derivatives (acid, esters, amides), particularly in aqueous solution and in supercritical CO_2 (eq. 3).

$$CO_2 + H_2 + HZ \longrightarrow HC(O)Z \ (Z = OH, OR, NR_2) \qquad (3)$$

Attractive undeveloped processes are conversions of CO_2 to more complex organic products containing C-C bonds. In this category are reductive coupling of CO_2 to C2 products such as ethylene glycol (eq. 4).

$$2\,CO_2 + 5\,H_2 \longrightarrow HOCH_2CH_2OH + 2\,H_2O \qquad (4)$$

Carboxylations: Status and Challenges

Attractive for chemicals production are non-hydrogenative processes in which CO_2 is added to organic substrates to form carboxylated products. Thermodynamically favorable, established, but little studied conversions include the co-polymerization of CO_2 with epoxides to give polycarbonates and additions to alkynes to yield pyrones and polypyrones. Carboxylation reactions using CO_2 may also provide an environmentally benign alternative to phosgene-based processes. A desirable, albeit thermodynamically challenging, process for CO_2 conversion would involve the carboxylation of C-H bonds, affording either formates or carboxylic acids (eq. 5).

$$R_3C\text{-}H + CO_2 \longrightarrow R_3C\text{-}O_2CH \text{ and/or } R_3C\text{-}CO_2H \qquad (5)$$

Although much is known about carboxylation processes involving M-H, M-OR, M-R, M-olefin and M-acetylene functionalities to provide C-H, C-O and C-C bond formation, there are still many mechanistic aspects of these reactions which require serious investigations. These include the following: a) Regiochemical control of the carboxylation process involving R-M-H intermediates, possibly generated via alkane activation. C-H bond formation is generally much faster thermally than C-C bond forming processes; however, preliminary experiments support the notion that C-C coupling can be greatly accelerated by way of photolysis. A key issue is how to selectively obtain $R\text{-}CO_2\text{-}M\text{-}H$ rather than $R\text{-}M\text{-}O_2CH$ species. b) CO_2 insertion into M-H bonds affords formates; at this point, it does not appear possible to control the regiochemistry of the insertion to give M-COOH rather than $M\text{-}O_2CH$. This is an issue of relevance to biomimetic analogs. Furthermore, the

homogeneous transformations of metal formates leading to more reduced carbon species are virtually unknown. c) Metal-olefin/CO_2 coupling reactions are known which lead to C-C bond formation, *i.e.*, reaction 6.

$$\text{M-olefin} + CO_2 \longrightarrow \text{M-OC(O)CH}_2\text{CH}_2 \qquad (6)$$

Is it possible to design a system in which the regiochemistry of the insertion reaction yields M-C and O-C(alkyl) bond formation? d) Although catalysts for CO_2/epoxide copolymerization are known, there is much room for development of better catalysts for the process, in particular, catalysts for living polymer systems. In addition, there is a need for catalysts that will effectively couple CO_2 and other organic substrates leading to polymerization. It is of importance to note that polymers possessing CO_2 in the backbone are biodegradable. e) In all processes described above, photochemical or electron-transfer enhancement or alterations in reaction pathways are worthy of study.

Redox (O-transfer) Processes and Challenges

Finally, one may consider various CO_2 splitting schemes which produce CO and, in some cases, value added oxidized organic co-products (eq. 7a,b).

$$CO_2 \longrightarrow CO + 1/2\ O_2 \qquad (7a)$$

$$CO_2 + \text{Sub} \longrightarrow CO + \text{Sub-O} \qquad (7b)$$

The first of these (7a) involves direct CO_2 splitting, an endergonic process of interest for energy storage and, when coupled with existing technologies for CO conversion, of potential value in CO_2 recycling to organics. Transition metal-promoted half reactions accomplishing (8a) have been reported (*e.g.*, $CO_2 + M \longrightarrow MO + CO$; $MO + h\nu \longrightarrow 1/2\ O_2$) but further reactivity and mechanistic studies are needed before practical catalytic systems can be designed. A few examples of type (7b) processes have been reported with easily oxidized substrates (*e.g.*, phosphines, isocyanides) but mechanistic details are lacking. Extension of such reactions to synthetically more important substrates such as olefins (to make epoxides) or alcohols (to ketones) is highly desirable and (because of thermodynamics constraints) may benefit from photochemical promotion.

Fundamental Reactivity Studies- Status and Prospects

Mechanistic and reactivity studies of the interaction of CO_2 with transition metal complexes are critical to new developments in thermal and photochemical CO_2 conversion. Such studies will: (1) help elucidate the mechanisms of existing catalytic reactions of CO_2; (2) improve their selectivity and efficiency; and (3) provide a basis for the discovery of new, useful CO_2 conversion processes.

Metal-coordinated carbon dioxide complexes presently known involve carbon-bound CO_2 ligands; one or both oxygens may be bound to metal centers also. Furthermore, electron-rich metal centers

are required to bind the weakly electrophilic CO_2. Once bound, the resulting bent CO_2 ligand is activated as a nucleophile (toward CO_2, protons, carbon and metal electrophiles and toward coordinated alkenes). Also, oxygen transfer reactions have been observed (to CO_2 to form carbonate and CO and to coordinated CO). Efforts to make synthetic uses of the oxygen transfer reactions, for example epoxidation reactions, are needed.

A variety of bonding types of a single CO_2 ligand have been identified, involving bonds to as many as four metal centers (or metal + hydrogen bonds) and the spectral characteristics of these are known. In some cases, the spectral characteristics show dependence on the coordination geometry of the metal center which binds the carboxyl oxygens. The relationship of these structural parameters to the reactivity of coordinated CO_2 are not known.

Reactions in Supercritical CO_2

Other considerations which deserve serious investigation include mechanistic studies carried out in super critical CO_2, where carbon dioxide serves as both solvent and reactant. Relevant to these studies are concurrent development of synthetic methodology of a large variety of ligands which are soluble in super critical CO_2, *e.g.*, ligands containing perfluoro-tails. Concomitant with these investigations should be the development of techniques for spectroscopic probing of reactions carried out in super critical CO_2.

Electrochemical CO_2 Reduction

Electrochemical reduction of CO_2 is concerned primarily with the development of catalysts (either homogeneous or heterogeneous) that enable the efficient use of electrons to reduce CO_2. Direct electron transfer to CO_2 occurs with large overpotentials (typically between 1 and 2 V) and produces a limited range of products. Development of catalysts can significantly reduce the potentials required for CO_2 reduction and channel the reaction to give a single desired product. Coupling photochemical electron transfer with electrochemical CO_2 reduction catalysts can lead to useful light-driven CO_2 reduction systems. The electrons used in the reduction may be produced by electron transfer following excitation by light of molecular photosystems, semiconductor particles, semiconductor electrodes, or photovoltaic devices.

A number of electrochemical CO_2 reduction systems have been reported. Reduction can be carried out directly at Cu electrodes to yield a range of products including formate, methanol, methane and C2 products. Macrocyclic metal complexes and metal phosphine complexes catalyze the electrochemical reduction of CO_2 to CO or formate. Bipyridyl and terpyridine complexes catalyze the reduction to CO, formate, formaldehyde, and methanol depending on the catalyst and reaction conditions. Electrochemical CO_2 incorporation into various alkynes has been achieved to produce α,β-unsaturated acids using $[Ni(bpy)_3]^{2+}$ complexes with Mg electrodes. C2 species such as HOH_2CCOOH and HC(O)COOH are produced together with CO and formic acid with a Ru complex at -20 °C. However, none of these systems combines the desired properties of high rate, good product selectivity, high catalyst stability and low overpotential that are required for a practical

catalytic system. Many of the known reduction systems exhibit one or more of these desirable traits, but none fulfill all of the criteria in a single system. Research is required to identify the fundamental properties that control the rate, selectivity, reduction potential, and stability of CO_2 reduction catalysts.

The rate determining step or steps for most electrochemical CO_2 reduction catalysts are not known. From those systems that have been studied in detail it is clear that the rate-determining steps are different depending on the particular catalytic system being studied. Rate determining reactions that have been identified include the reaction of the reduced species with CO_2, cleavage of the C-O bond in CO_2 to form CO, and insertion of CO_2 into M-H bonds. As systems capable of reducing CO_2 beyond the two-electron stage become more fully developed it is likely that other rate-determining reaction steps will be identified. It is important that structure-activity relationships that control these different rate-limiting steps be understood so that faster catalysts can be designed in a rational manner.

Carbon dioxide can be reduced to a variety of possible products, including CO, formate, formaldehyde, methanol and methane as well as C2 products. Multiple electron transfers and protonations are required to obtain these products. Transition metal complexes are well-suited to catalyze these transformations because they 1) provide a range of accessible oxidation states, 2) are able to carry out multiple electron transfers and 3) are capable of stabilizing intermediates along the course of the reduction process. The majority of the known catalytic systems produce two-electron reductions. In many of these systems more than one product is formed, *i.e.*, CO, formate, and hydrogen. A knowledge of mechanistic details, general structure-activity relationships, and solvent effects is needed to permit selection for one product channel over another. Highly selective catalysts will reduce the need for product separation and purification. A second major issue in catalyst selectivity is the reduction of CO_2 beyond the two-electron stage. Although a few systems are known in which CO_2 is reduced by four, six, and even eight electrons, the mechanistic details are not understood. Increased efforts to synthesize and identify new catalytic systems capable of reducing CO_2 beyond CO and formate are needed, as well as an increased mechanistic understanding of those systems known to carry out four, six and eight electron reductions. For multi-electron reductions, strategies for storing electrons on the catalyst may be important. Two possibilities that are currently being pursued are to use multimetallic catalysts and catalysts with ligands capable of storing reducing equivalents such as bipyridine or quinones.

It is important that the reduction of CO_2 be carried out at a potential as close to the thermodynamic potential as possible in order to make the energy efficiency of the process as high as possible. This should guide the development of new catalysts and efforts to reduce the overpotentials of existing catalysts should be pursued. This will require the development of quantitative relationships between redox potentials for various metals that accounts for donor sets, coordination number, and geometry.

Catalyst stability is an important issue for both homogeneous and heterogeneous catalysts. For processes aimed at producing significant quantities of chemicals or fuels, turnover numbers ranging from 10^4 to 10^7 or 10^8 will probably be needed for chemicals and fuels respectively. The nature of

the deactivation processes for various catalysts needs to be delineated. Only in a few cases have the decomposition products or the nature of the deactivation process been fully identified. This information is needed before systematic approaches can be taken to improve catalyst stability or develop logical strategies for *in situ* catalyst regeneration. Relationships need to be developed between catalyst structure and the decomposition products observed, and mechanistic understanding of these pathways will be useful.

Summary Assessment and Potential Impacts on Technology

The successful development of processes for photochemical reduction of CO_2 to fuels and chemicals will require significant advances in our understanding of both photochemical and catalytic processes. The goals of research in this area are: 1) the development of efficient and stable photosensitizer/photocatalyst (*i.e.* solar light absorbers with long-term photostability); 2) basic study of photophysics and photochemistry of excited-states of molecules; 3) further understanding of photochemical processes including photo-induced electron/hole transfer and charge separation; 4) the development of thermal, elctro- and photo-catalysts for CO_2 reduction with a high catalytic activity and a low thermodynamic driving force; 5) efficient coupling between charge separation and thermal reaction; 6) combining oxidizing and reducing cycles; 7) mechanistic and kinetic studies including thermal and electrochemical CO_2 reduction. The range of knowledge required to obtain these goals makes it essential that a broad perspective toward CO_2 reduction processes be maintained. Contributions from a range of disciplines including photochemistry, synthesis, electrochemistry, and mechanistic chemistry will be needed. These disciplines are complementary and synergistic, and collaborations should be encouraged whenever possible. For example, it is relatively easy using electrochemical techniques to obtain thermodynamic data that is useful for developing photochemical processes. The kinetic data generated using photochemical, electrochemical, or normal spectroscopic techniques can be used as internal checks to gain greater insights and reliability in mechanistic studies. The mechanistic and kinetic data obtained by electrochemical and thermal reactions may provide a rational basis for the photoproduction of desired products. The development of new catalysts and structure-activity relationships will require synthetic, structural, and mechanistic studies. In short, a balanced approach to research will be required to achieve the goal of photochemical reduction of CO_2 to a broad range of carbon-based products that are in current use or that will be used in the future.

In assessing future impacts on technology, it is not clear which of the approaches to the reduction and/or incorporation of CO_2 into fuels and chemicals will have the most immediate impact. While CO_2 is abundant as a carbon source, it is a relatively dilute component of the atmosphere. Advances in separations technology will be needed to render CO_2 from the atmosphere as a viable carbon source for the production of chemicals and fuels. However, for incorporation into chemicals, CO_2 from natural gas deposits or recoverd from power plants could be employed. Possible use of CO_2 as a replacement for toxic reagents such as phosgene has considerable appeal from environmental and safety vantage points, but the chemistry remains to be developed. New materials in which CO_2 has been incorporated into a polymer backbone may possess properties that are unique or advantageous, *e.g.*, biodegradability. The ability to provide energy photochemically or

electrochemically to enhance the reactivity of CO_2 may result in new processes for chemicals production that are not energetically feasible using more traditional thermal reactions. Examples include the electrochemically driven carboxylation of alkynes and aromatic halides to carboxylic acids. The photochemical production of fuels will be inherently more complicated because: 1) it will likely involve the coupling of photochemical processes with electrochemical or thermal reactions; 2) fuels must be produced with much greater energy efficiency than is required for chemicals; 3) the catalyst selectivity and turnover numbers must be orders of magnitude higher for fuel production compared to chemical production. All of these factors indicate more stringent and demanding requirements for fuel production catalysts and photosynthetic systems based thereon. However, liquid and gaseous fuels based on carbon offer many advantages over alternative methods for storing energy due to their high energy density and ease of handling.

PANEL B-2

SOLAR HYDROGEN PRODUCTION

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Summary

This panel addressed different methods for the photoassisted dissociation of water into its component parts, hydrogen and oxygen. Systems considered include PV-electrolysis, photoelectrochemical cells, and transition-metal based microheterogeneous and homogeneous systems. While none of the systems for water splitting appear economically viable at the present time, the panel identified areas of basic research that could increase the overall efficiency and decrease the costs. Common to all the areas considered was the underlying belief that the water-to-hydrogen half reaction is reasonably well characterized, while the four-electron oxidation of water-to-oxygen is less well understood and represents a significant energy loss. For electrolysis, research in electrocatalysis to reduce overvoltage losses was identified as a key area for increased efficiency. Non-noble metal catalysts and less expensive components would reduce capital costs. While potentially offering higher efficiencies and lower costs, phòtoelectrochemical-based direct conversion systems undergo corrosion reactions and often have poor energetics for the water reaction. Research is needed to

understand the factors that control the interfacial energetics and the photoinduced corrosion. Multi-photon devices were identified as promising systems for high efficiency conversion. Research needs to be done to tailor these devices for the water splitting reaction. Microheterogeneous and homogeneous systems benefit from the knowledge base in electrochemistry and homogeneous and heterogeneous catalysis. For more efficient solar conversion, photosensitizers with desired lifetimes and redox potentials that make greater use of the entire solar spectrum need to be developed. The dark and possibly photo-catalyzed reactions that follow the initial light-induced charge separation need further study so the barriers to efficient splitting of water can be overcome. Surface modification of electrodes or dispersed systems by attachment of metal complexes capable of undergoing multi-electron or atom transfers can enhance the coupling of the charge separation process to the reactions leading to desired products. Water-stable hydride complexes and carbon nanotubes were identified as a possible means for separating hydrogen and oxygen in systems where both gases are evolved. Instead of generating oxygen, the oxidation half reaction accompanying hydrogen photogeneration could have application in chloride and sulfide oxidation and the destruction of atmospheric pollutants.

Overview and Other Sources of Information

Current interest in using solar energy for hydrogen production can be traced to the so-called "energy crisis" of the early 1970's and, more specifically, to the paper by Fujishima and Honda (1) describing photoelectrochemical generation of hydrogen and oxygen from water. Many of the issues relating to the widespread use of hydrogen as a commercial fuel were summarized in the plenary lecture by Tomkiewicz (2). In addition, several review articles have appeared recently that summarize research activities over the past 20+ years in the area of solar hydrogen production (3-6). There are also publications prepared by the Department of Energy describing various aspects of hydrogen production and utilization (7).

Panel B-2 considered the following approaches to solar hydrogen production:

- Photovoltaic or Photoelectrochemical Solar Cells Coupled to Water Electrolyzers
- Photoelectrolysis Systems
- Photochemical Homogeneous and Microheterogeneous Systems
- Photobiological Systems

The first three types of systems were considered in some detail. Scientists familiar with photobiological systems participated in Workshop Panel C, "Photosynthesis, Chemical Dynamics and Biofuels." Panel C's report should be consulted for information concerning progress and research needs in the area of photobiological systems. In his review (6), Bolton has suggested that Photodegradation Systems should also be considered as a potential hydrogen production process. Photodegradation systems were discussed briefly by Panel B-2; for a more in depth discussion the report Panel B-3, "Photodetoxification and Purification of Water and Air" should be consulted.

Figure 1 contains a general scheme describing all of the proposed systems for the generation of hydrogen using light. Water is the only realistic source for massive, commercial production of hydrogen. However, other sources (e.g. H_2S, HCl, HBr, HI etc.) should be explored especially if the hydrogen generation is coupled to other specialized needs (for example, H_2S removal from sulfur-rich coal). All systems include a **Light Absorber** that produces electrons and holes (electron vacancies) from solar photons. In order to avoid back-reactions (e.g. recombination), each process also contains a mechanism for **Charge Separation** that allows the electrons and holes to be separated spatially. Because of the mismatch between the number of electrons and holes transferred in the steps described above and those needed for the generation of products, **Catalysts** are needed to reduce the water to H_2 and to evolve O_2 (or some other oxidized species).
Although there are clearly certain similarities between the four approaches considered, there are some important differences as well. For the systems in which the light absorber is a semiconductor, the charge separation mechanism is usually an intense electric field present in the material. For molecular and biological systems, charge separation occurs via a series of energetically downhill

electron transfer reactions. There are also large differences between the separation distances at which light absorption occurs and where H_2 and O_2 are evolved in the various systems. For the systems coupled to water electrolyzers, light absorption, which results in production of electricity, and the electrolyzer can be separated by many meters. For the electrolyzer and photoelectrolysis systems, generation of the two products is spatially separated across impermeable barriers. For the photochemical homogeneous and microheterogeneous and the photobiological systems these distances are much shorter (1 to 100 nm) resulting in co-generation of the products. These differences become important in the overall design of the system in terms of how the hydrogen and oxygen are collected, separated and stored.

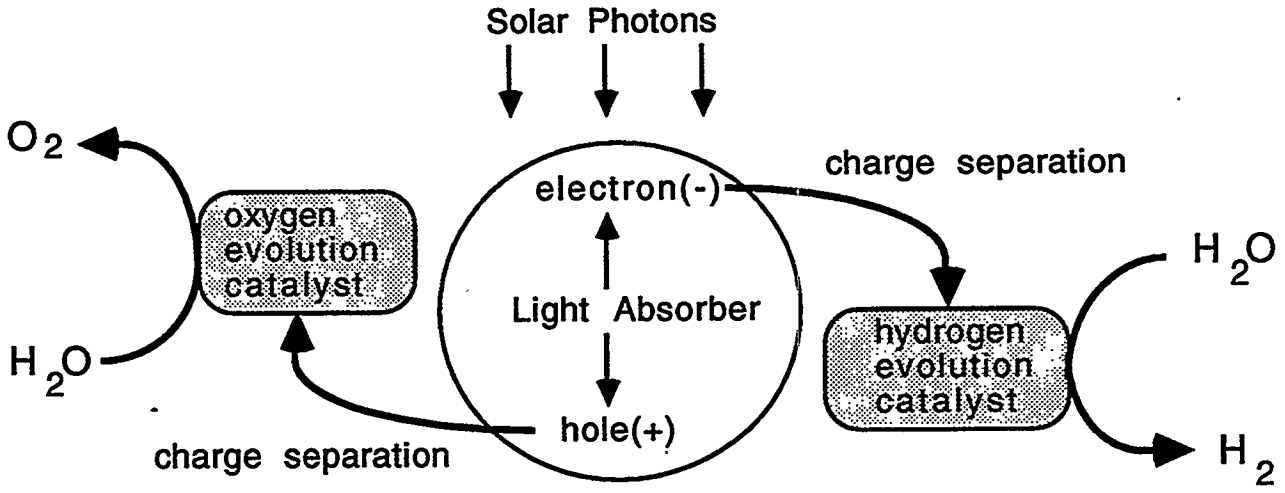


Figure 1. General Scheme Depicting Processes Involved in Solar Hydrogen Production

For both semiconductor- and molecular-based systems, there exists a reasonably sound understanding of the factors that control the absorption of solar photons, the lifetime of electronically excited states, and charge separation processes. Their dependences on distance, energy, medium and temperature are reasonably predictable. Inhibition of the back reactions associated with various steps in the overall process can be achieved using a variety of micro-environments, as long as a portion of the initial photon energy can be sacrificed. Reducing the rate of the back reaction without these energy losses is still a challenge. The mechanisms for H_2 generation on noble metal and molecular catalysts are reasonably well understood. Rates, intermediates and their dependence on external parameters have been determined. The evolution of oxygen is far less well understood.

A generic goal of all solar hydrogen production systems is to achieve a high efficiency for conversion of solar energy into stored hydrogen fuel. The Scheme shown in Figure 1 is highly simplified and does not adequately depict the details of systems that utilize multiple absorbers and electron transfer pathways. The limiting, theoretical efficiencies for many of these pathways have been calculated. Methods for reporting experimental efficiencies that facilitate direct comparisons between systems and with theoretical limits have been suggested (6).

Present Status of Solar Hydrogen Production Systems and Selected Ongoing Research Activities

Photovoltaic or Photoelectrochemical Solar Cells Coupled to Water Electrolyzers

Water electrolyzers are electrochemical cells that use an external power source to convert water into hydrogen and oxygen. If the external power is produced using photovoltaic (PV) cells or regenerative photoelectrochemical (PEC) cells, such systems represent a straightforward approach to solar hydrogen production. Photovoltaic systems coupled to electrolyzers are commercially available but are presently not economically competitive with nonrenewable methods for producing hydrogen such as reforming methane. Issues related to lowering costs of solar generated electrical power are discussed in the reports from Panels A-1 (Photochemical and Organic-Based Solar Cells) and A-2 (Solid State Photochemistry). Current commercial water electrolyzers suffer from high capital costs which contribute to the cost of (photo)electrolytically produced hydrogen. Therefore, improvements in water electrolyzers, especially those designed to utilize solar electrical power, could lower the costs for producing hydrogen via this route.

Photoelectrolysis Systems

Direct photoelectrochemical water-splitting, also known as photoelectrolysis, represents an advanced alternative to PV or PEC/electrolyzer system. Photoelectrochemical water-splitting is the process where an illuminated semiconductor immersed in an aqueous solution is used to decompose water into its components, hydrogen and oxygen. Light, incident on a semiconductor electrode, splits water directly with no external current flow. Such a one-step monolithic system eliminates the need to generate electricity externally and subsequently feed it to an electrolyzer. Combining the electrolyzer with the PV system eliminates one of the high cost components of a PV-electrolysis hydrogen generation system. Since external wiring is not used, only the piping necessary for the transport of hydrogen and oxygen to external storage systems or gas pipelines is required. This type of monolithic system also reduces semiconductor processing since surface contacts, interconnects and wiring are no longer necessary (see Figure 2).

For a one-step process to be viable, the light harvesting system must generate enough voltage to decompose water, and the system must be stable in a water environment. At 25°C, splitting water into hydrogen and oxygen requires a voltage of 1.23 V. At current densities for solar applications, typical values of the overvoltage for the hydrogen evolving and oxygen evolving reactions are 50 mV and 275 mV respectively. A potential, then, of at least 1.6 V is required for a water splitting system. For a single gap semiconductor-based direct conversion water-splitting system, the requirement of at least 1.6 V added to the internal losses from the semiconductor, means a minimum bandgap of 1.8 electron volts. The entire spectrum of visible light can be used for water splitting. Metal catalysts are required on both the hydrogen and oxygen evolving surfaces to speed up the redox reactions and stabilize the semiconductor. An additional requirement is that the semiconductor band edges span the redox potentials of both the hydrogen and oxygen evolution reactions. Most well-known semiconductor electrodes are unsuitable for photoelectrolysis since they have too large a band gap

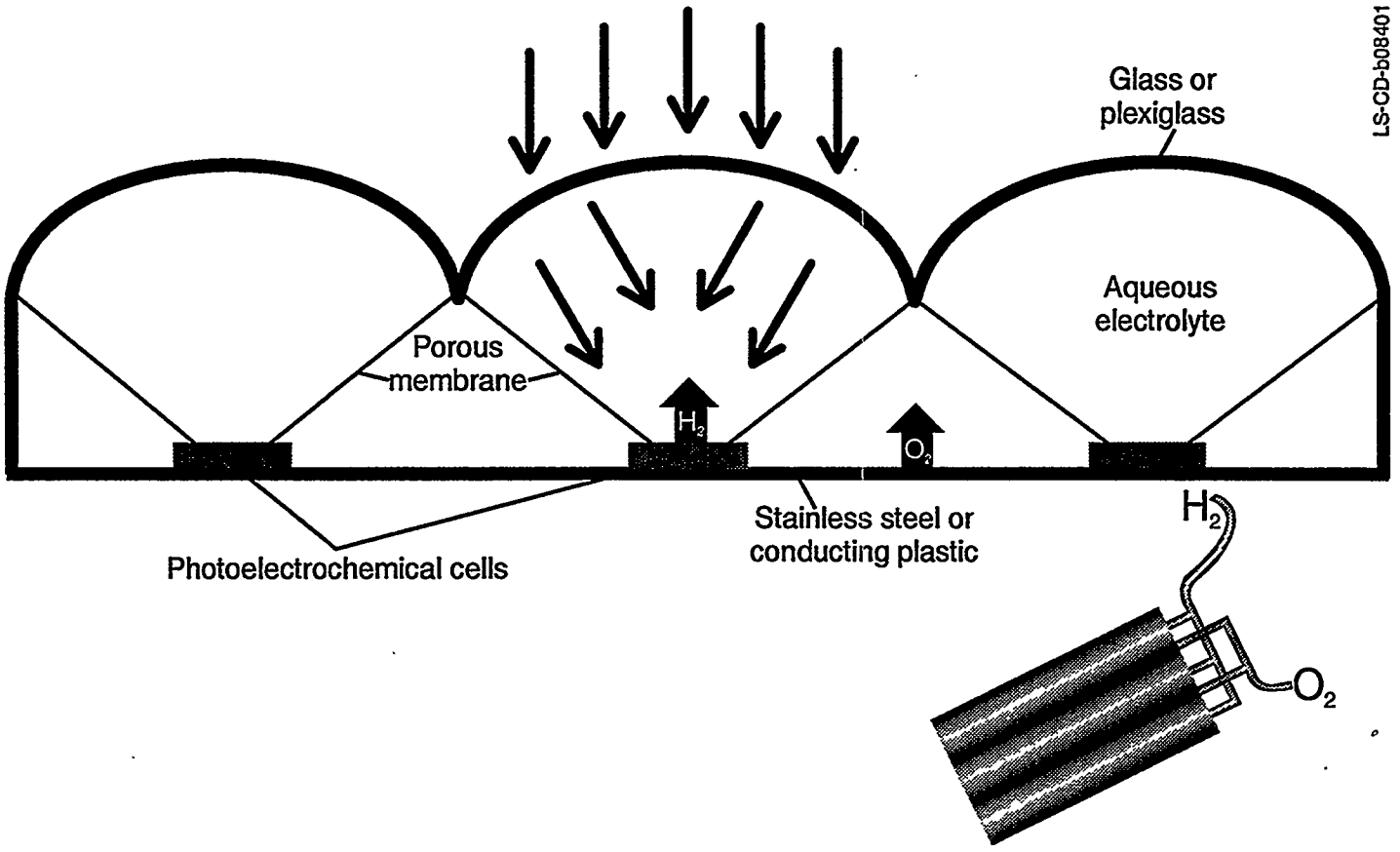


Figure 2. Conceptual Design of a Water Splitting System with Light Concentration

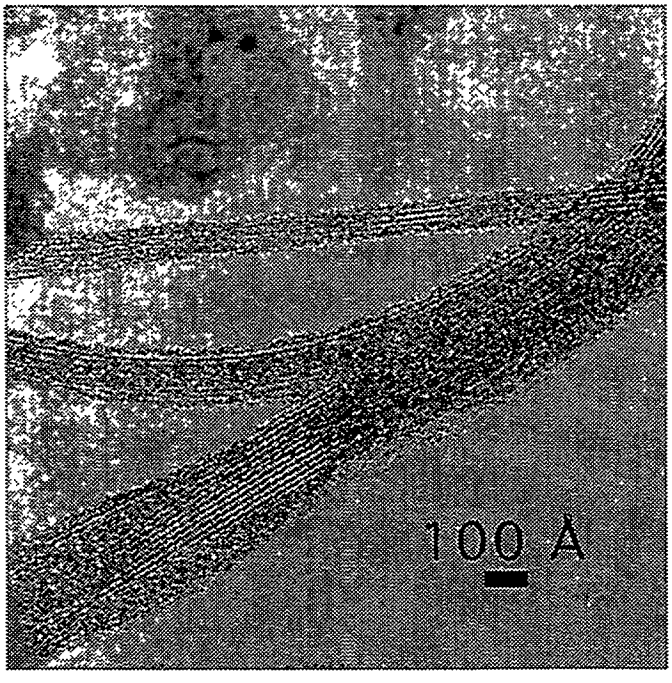


Figure 3. Transmission electron microsope image of bundles of 12 Å diameter single-wall carbon nanotubes.. (imaging by K.M. Jones at NREL)

and absorb very little light, leading to low efficiency, or too small a bandgap and do not generate sufficient voltage, or have stability problems, or have band edges that do not span the redox potentials of both the hydrogen and the oxygen evolution reactions.

An approach to developing a direct photoelectrochemical water-splitting system being explored by researchers at NREL is to use the best semiconductor materials that are available, consistent with the energy requirements for water splitting and stability in an aqueous environment. The efforts are directed at two promising semiconductor systems; III-V semiconducting materials (materials are made with various combinations of gallium, indium, arsenic and phosphorus), and amorphous-silicon based systems. The III-V semiconductors are the focus of solid-state research groups for the next generation of high efficiency solar cells. These include single bandgap systems and multiphoton devices (tandem cells). The investigations of $GaInP_2$ have shown that, while its bandgap (1.8–1.9 eV) is optimum for water electrolysis, the band edges are 300–400 mV too negative and therefore do not straddle the hydrogen and oxygen redox levels. Part of the work is directed at modifying the surface of $GaInP_2$ in order to produce a more energetically favorable band edge. Some surface treatments are beneficial in improving the energetics. The surface of the GaAs was modified with tetra(4-pyridyl)porphyrinatomaganese(III) using 3-chloropropyltrimethoxysilane as a coupling agent. The onset of photocurrent for the derivatized electrode was shifted positively by up to 180 mV with respect to the unmodified electrode. This is the first experimental evidence showing that covalent attachment of positive charges to semiconductor surfaces will shift the band edges to positive potentials. Since the GaAs surfaces are similar to those of $GaInP_2$, this work may be transferable to $GaInP_2$.

Photovoltaic tandem cell technology connects photovoltaic layers (p-n junctions) with different semiconductor bandgaps in series, one behind the other, in a single monolithic device. This arrangement provides the highest theoretical conversion efficiency of any photoconversion system. In NREL's initial work on the $GaInP_2$-based tandem cells, hydrogen and oxygen appear to be co-evolved from the illuminated surface. While the exact mechanism of the water decomposition process is not fully understood at this time, the phenomenon evidently arises from oscillations in the device caused by a lack of current matching between the upper and lower devices. The tandem cells were modified by increasing the thickness of the p-$GaInP_2$ layer in the top cell to greater than 1.5 μm (typical thickness is 0.7 μm or less). With the thicker p-layer, hydrogen was observed to be evolved from the illuminated surface, while oxygen was evolved from a separate electrode. While the $GaInP_2$/GaAs tandem cells represent a very high efficiency system, it will likely be a relatively expensive one. A less expensive alternative system is based on amorphous silicon (a-Si). There are two main technological problems that must be solved before an a-Si based system could operated as a photoelectrolysis device. 1) a-Si is not stable in contact with aqueous electrolytes, it decomposes within a few minutes, and 2) its bandgap is insufficient to effect the decomposition of water. Current state-of-the-art a-Si based devices address both of these problems. Multiple junction a-Si devices can have voltages greater than 1.8 volts, which is sufficient for water splitting, and cells are being developed which have a surface coating of amorphous silicon carbide (a-SiC). Preliminary work has shown that a-SiC provides a stable surface layer and is effective at protecting the underlying photovoltaic layers.

An alternative approach to using semiconducting materials that absorb visible light is the modification of stable, large band gap oxide materials such as TiO_2. One way that this can be accomplished is by sensitization using a suitable dye. Another way is by ion implantation. The absorption band of TiO_2 doped with Cr ions by ion implantation has been found to shift into the visible light regions; the extent depending on the amount of Cr ions implanted. Similar shifts in the absorption band were also observed by ion implantation of V, Ni, or Fe. Three-dimensional SIMS analysis of the metal ion implanted TiO_2 catalysts indicate that the metal ions are deeply injected up to a depth of 400-600 Å from the surface and highly dispersed within the TiO_2. Visible light irradiation (wavelengths > 450 nm) of metal ion-implanted TiO_2 catalysts led to various kinds of photocatalytic reactions including the direct decomposition of NO into N_2, O_2, and N_2O.

In addition to parameters constraining semiconductors, modification of the solution phase electrolyte in photoelectrochemical cells is often important for understanding and controling the mechanism and efficiency of energy conversion. Electrolyte modification of photoelectrochemcal systems can be used to: (i) enhance charge transfer; (ii) suppress competing reactions (e.g., electrode and electrolyte decomposition reactions); (iii) substantially affect the driving potential available for energy storage reactions. The fundamental importance of electrolyte modification, in terms of the distribution of species in photoelectrolytes and the pragmatic importance in terms of enhanced solar conversion, has been conveyed in studies on polysulfide, ferrocyanide, polyselenide and polyiodide electrolyte regenerative photoelectrochemical systems (9).

Photochemical Homogeneous and Microheterogeneous Systems

Transition metal complexes generally absorb strongly in the visible and their excited states are frequently long lived and capable of rapid electron transfer. In addition, the complexes are able to undergo the multi-equivalent changes generally required for the formation of highly reduced or oxidized species and can be designed to have vacant (or readily accessible) coordination sites for the binding (and activation) of intermediates. Transition metal complexes are thus ideally suited for use in systems capable of photogenerating fuels or other useful chemicals under homogeneous conditions (10). Amouyal has provided a recent, comprehensive review of this area (4).

Thermodynamic Considerations

One- and two-electron potentials (vs. NHE) for reduction of H^+ at pH 7 and 25 °C are summarized below. The standard state is 1 atmosphere for H_2 and 1M for the other species.

$2\,H^+ + 2\,e^- = H_2$	-0.41 V
$H^+ + e^- = \cdot H$	-2.69 V
$\cdot H + e^- = :H^-$	+0.03 V
$H^+ + 2\,e^- = :H^-$	-1.33 V

In principle, all couples with reduction potentials below that of the H_2O/H_2 couple (-0.41 V at pH 7) are capable of reducing water to hydrogen. However, in practice, such reactions generally proceed

extremely slowly in the absence of a suitable catalyst. As is evident from the above potentials, the one-electron step to produce a free hydrogen atom (or the two-electron step to produce a free hydride ion) is energetically very unfavorable. Thus the primary H^+ reduction products $\cdot H$ or H^- need to be stabilized in order for the reaction to proceed at a reasonable rate. Studies of homogeneous hydrogen-formation reactions and their reverse, hydrogen activation, mediated by a variety of metal complexes have shown that metal hydride (and possibly H_2) complexes are important intermediates.

Some Homogeneous and Microheterogeneous Systems

A homogeneous system for hydrogen formation that has been studied in some detail consists of RuL_3^{2+} (L = 4,4'-$(CH_3)_2$bpy), triethanolamine (TEOA), and $Co(bpy)_3^{2+}$ in 50% aqueous CH_3CN (11). Upon irradiation with 450 nm light this system produces hydrogen with a quantum yield of 0.29 under optimum conditions. The excited $*RuL_3^{2+}$ is oxidized by $Co(bpy)_3^{2+}$ to produce RuL_3^{3+} and $Co(bpy)_3^{+}$. The subsequent hydrogen generating reactions are very efficient because the optimal quantum yield (0.29) is close to the cage escape yield of $Co(bpy)_3^{+}$ (0.27). A similar system, based on the reduction of $*Ru(bpy)_3^{2+}$ to $Ru(bpy)_3^{+}$ by ascorbate, has also been described (12). The cobalt(I) species and the cobalt(III) hydride complexes formed from them are very reactive. In addition to mediating the generation of H_2 and the reduction of bpy to $bpyH_2$, they also reduce CO_2 to CO (13-15). In effect, the $RuL_3^{2+}/Co(bpy)_3^{2+}$/TEOA system is capable of producing "synthesis gas" (CO + H_2). Use of $Ru(bpy)_3^{2+}/Co^{II}(dmgH)_2$ (dmgH = dimethylglyoxime) in a DMF/TEOA medium yields only H_2 even in the presence of CO_2 (16). (It is proposed that the more powerful and longer lived reducing agent $Ru(bpy)_3^{+}$, $E_{1/2}$ = -1.28 V vs NHE, rather than $*Ru(bpy)_3^{2+}$, $E_{1/2}$ = -0.84 V, is the electron donor for the $Co^{II}(dmgH)_2$, $E_{1/2}$ = -0.95 V.) Conversely, the reduction of CO_2 to formate without the simultaneous reduction of H_2O to H_2 occurring to any significant extent can be accomplished by using $Ru(bpy)_3^{2+}$ as the photosensitizer and catalyst precursor in a DMF/TEOA medium (the catalyst is a $Ru(bpy)_2^{2+}$complex, probably *cis*- $Ru(bpy)_2(CO)Cl$) (17,18). Similarly, the reduction of CO_2 to CO without significant reduction of H_2O to H_2 can be effected by using $Re(bpy)(CO)_3Cl$ as both the photosensitizer and the homogeneous catalyst in a DMF/NTE (nitrilotriethanol) medium (19). Evidently, although similar intermediates are formed in H_2 generation and CO_2 reduction, their specificities vary.

The $Co(bpy)_3^{2+}$-based system exhibits both important similarities and differences with the analogous $Ru(bpy)_3^{2+}/Rh(bpy)_3^{3+}$/TEOA system (20,21). Irradiation of the rhodium-based system at pH 7-8 in the absence of platinum yields rhodium(I) and free bpy but no H_2. In the presence of colloidal platinum, H_2 and very little free bpy are produced. Contrary to the original proposal that the H_2 was produced in platinum-catalysed reactions of rhodium(I) (22), detailed mechanistic studies showed that the platinum-catalyzed reactions of rhodium(II) were responsible for the hydrogen formation (21). In the presence of platinum the $Rh(bpy)_3^{2+}$ produced reduces H_2O/H_3O^+ to hydrogen with a quantum yield of 0.11, close to the cage escape yield of the primary products (0.15). Evidently the reactions that convert the reduced complex to hydrogen are remarkably efficient in both the cobalt- and rhodium-based systems. The efficiencies of both systems decline on prolonged photolysis due to the formation of reduced bipyridine.

The mechanism for hydrogen production in the rhodium-based system strongly resembles that in the well-studied microheterogeneous $Ru(bpy)_3^{2+}$/methylviologen (MV^{2+}, 1,1'-dimethyl-4,4'-bipyridinium dication)/TEOA (or EDTA)/colloidal Pt systems with $Rh(bpy)_3^{2+}$ fulfilling the role of the MV^+ radical (4,23). In this respect the rhodium-based system offers no particular advantage over other hydrogen-photogeneration systems requiring heterogeneous catalysts. Indeed the rhodium system is more expensive than systems based upon methylviologen. Like the rhodium system, the methylviologen-based systems are subject to efficiency-lowering side reactions, mainly hydrogenation of MV^{2+} via the protonated viologen radical (4). Considerable improvement in the efficiency of the system is obtained by using tetramethyl- or hexamethylviologen or other structurally modified viologens as quenchers (24,25) and by using the triplet state of 9-anthracenecarboxylate, formed either by direct photo-excitation (26) or by energy transfer from $*Ru(bpy)_3^{2+}$, as the primary electron donor (27).

In the systems considered above $*Ru(bpy)_3^{2+}$ is oxidized by a metal complex or by methylviologen to yield $Ru(bpy)_3^{3+}$ which is then reduced by a sacrificial electron donor (TEOA or EDTA). In the "water splitting" reaction, eq 1, water itself serves as the sacrificial donor ($\Delta G^\circ = 56.7$ kcal/mol of H_2O or 1.23 eV/e). In effect, water is both reduced to hydrogen and oxidized to oxygen.

$$\begin{aligned} 2\,H_2O &\rightarrow 2\,H_2 + O_2 \\ 4\,H_2O + 4\,e^- &= 4\,OH^- + 2\,H_2 \\ 2\,H_2O &= 4\,H^+ + O_2 + 4\,e^- \end{aligned} \qquad (1)$$

Although reduction of $Ru(bpy)_3^{3+}$ by hydroxide to form $Ru(bpy)_3^{2+}$ and oxygen is thermodynamically favorable, the reaction is accompanied by ligand degradation (28). Oxygen formation is considerably enhanced in the presence of Co^{2+} (29-32) or by trapping the $Ru(bpy)_3^{3+}$, for example, in Zeolite-Y (33). A homogeneous system consisting of tris-(1-(4-methoxyphenyl)-2-phenyl-1,2-ethylenedithiolato)tungsten and MV^{2+} in acetone-water has been reported to produce H_2 and O_2 with a 4% quantum yield in the visible (400 - 500 nm) (34). This is an important result which should be independently confirmed.

An important aspect of many homogeneous and microheterogeneous photochemical systems is the nature of the coupling between the various components. Various polymeric structures appear to hold promise in their ability to shuttle charges between absorbers and catalyts. Peptide structural motifs containing proline and alpha helices have been assembled and display unexpectedly rapid intramolecular electron transfer at long distances. These structures are currently being used to link Ru and Ir complexes to metal electrodes in order to study heterogeneous charge transfer processes. Another system under study involves the preparation of conjugated polymers, such as polyazobipyridine, that contain metal coordination sites at fixed distances along the polymer backbone. It should be possible to incorporate many of the interesting metal complexes discussed above into these polymeric structures.

The Water Gas Shift Reaction

The water gas shift reaction (WGSR) affords another route to hydrogen formation. In this system CO rather than H_2O acts as the electron donor and CO_2 rather than O_2 is produced (eq 2).

$$H_2O + CO \rightarrow H_2 + CO_2 \quad (2)$$

The reaction is thermodynamically favorable ($\Delta G^\circ = -4.75$ kcal/mol) and is catalyzed by a variety of metal complexes (35,36).

The use of light permits certain WGSR's to be run under extremely mild conditions. For example, the reaction can be carried out at room temperature, ambient pressure, and neutral pH by using the iridium(III) complex $[(Me_5C_5)Ir^{III}(bpyRR' \text{ or phen})X]^+$ (X = H, Cl) and visible light (37). Key steps in the photocatalyzed reaction are the elimination of CO_2 and H^+ from a hydroxycarbonyl iridium(III) intermediate to form an iridium(I) complex which undergoes protonation to yield the iridium(III) hydride (alternatively the hydride may be formed directly in the decarboxylation of the hydroxycarbonyl). The reaction of the excited iridium(III) hydride with protons reforms the starting iridium(III) complex and hydrogen. The use of light may find important application in other reactions involving hydrides.

Conclusions

A fairly detailed understanding exists regarding the mechanisms obtaining in homogeneous systems that yield hydrogen upon irradiation with visible light. Unfortunately, most of the characterized systems require a sacrificial donor or acceptor, are subject to efficiency lowering side reactions, and make poor use of the entire solar spectrum. True, efficient water-splitting systems remain elusive. Nevertheless, the knowledge gained on the $H_2O \rightarrow H_2$ half reaction will very likely find application in a variety of systems. Moreover, as pointed out recently (3), water splitting may not necessarily represent the only economical solar energy conversion process. For example, photo-assisted brine splitting ($2H_2O + 2Cl^- \rightarrow 2OH^- + Cl_2 + H_2$) may well be useful in certain situations (3).

Hydrogen Recovery and Storage Systems

Due to safety issues associated with the flammability of gaseous hydrogen and to the problems associated with recovering hydrogen from co-generation systems, novel methodologies for selectively sorbing and reversibly storing hydrogen need to be developed. Solid-state storage as a hydride or by absorption (for example, in carbon, zeolites or by a metal complex) is safer and potentially more economical than compression or liquifaction. The use of nanoscale materials, which possess unique physical and chemical properties, merits investigation. Closed-cage carbon structures known as Fullerenes represent a distinct class of nanostructures which are formed by closure of curved van der Waals surfaces, and therefore, can be defect free. The Fullerenes are formed in balls, tubes, and nested structures and, in special cases, can be obtained in high yield either by purification, or by direct synthesis (38). Small-diameter (e.g. 12 Å) single-walled carbon

nanotubes are of interest due to the nanocapillary condensation phenomena that have been predicted for these materials (Figure 3). Researchers at NREL have developed methods for the routine production of soots containing small-diameter single-wall carbon nanotubes by the co-evaporation of cobalt and carbon in helium atmospheres. Transmission electron, scanning tunneling, and atomic force microscopy as well as Raman and infrared spectroscopies have been used to study the link between structure, synthesis parameters, and hydrogen adsorption in these materials. This work is on-going with the goal being the synthesis of nanonotube assemblies for high-energy-density storage of hydrogen (39).

Scientific Challenges / Important Areas For Future Research

Hydrogen is a commodity chemical and, at the present level of demand, can be produced inexpensively from non-renewable sources. Because solar energy is spatially diffuse at the earth's surface and therefore difficult to collect and utilize, it is not realistic to expect solar hydrogen production systems to be competitive in terms of cost with traditional sources at the present time. The goal of future research in this area is to develop the basic understanding associated with each type of approach that will allow hydrogen to be produced as a fuel when traditional sources become depleted, more expensive or not viable for environmental reasons. The panel believes that basic research associated with each of the types of systems identified is justified and should address one or more of the issues described below:

- Improved catalysts (homogeneous or heterogeneous) for the reaction involving the oxidation of water to oxygen is important for all solar hydrogen production systems. The focus should be on identifying catalysts and catalytic mechanisms that produce oxygen at low thermodynamic driving forces and that can couple effectively to photoinduced charge separation events.

- Efficient photoinduced water-splitting requires that the energies of electronic excited states be carefully matched to the redox energies associated with the hydrogen and oxygen evolution reactions. This matching is presently easier to control in a rational manner for molecular systems than for semiconductor systems. Further understanding of how bulk material, surface and electrolyte properties combine to determine band edge positions in photoelectrochemical cells is needed.

- The extension of the absorption bands for light absorbers capable of producing hydrogen from water (or other sources) further into the visible range continues to be an important challenge. Research areas include the preparation/characterization of more solar efficient molecular sensitizers and better methods for the doping of semiconductors.

- The long-term photostability in aqueous environments of the light absorber/charge separation components for all solar hydrogen production systems must be improved. For semiconductor-based systems, this might be accomplished by synthesis of new materials, surface modification of existing materials, or careful attention to the composition of

electrolyte solutions. For molecular-based systems, this might be accomplished by learning to control the factors that determine excited-state lifetimes, quenching reactions and photodissociation reactions.

- Microheterogeneous systems that combine molecular and semiconductor components (e.g., dye-sensitized semiconductors and solid surfaces modified with molecular catalysts) represent a wide range of possibilities for solar hydrogen production. However, the description, experimental and theoretical, of electron transfer across interfaces is far less well understood than for homogeneous systems. Similarly, the description of the solid-solid interface between the particles utilized in certain microheterogeneous systems needs to be better characterized and understood.

- Novel schemes for collecting, storing, and releasing hydrogen are needed, especially for production systems in which hydrogen and oxygen are co-generated. Possible research areas include preparation and characterization of novel nanostructures, such as carbon nanotubes, and the photochemistry of metal hydride complexes.

Impact of Solar Hydrogen Research on Other Technologies

Even though large-scale solar hydrogen production may not become economically (and socially) attractive until the 21st century, basic research related to this goal has already contributed to other technologies and will continue to do so in the future. For example, Fujishima and Honda's early paper on photoassisted water-splitting (1) sparked considerable interest in the properties and use of TiO_2. Many years of research on TiO_2 in the laboratories of Gratzel resulted in the development of the efficient photoelectrochemical solar cells described at the workshop (8). Much of the research discussed in Panel B-3, "Photodetoxification and Purification of Water and Air" involved TiO_2. Several companies have TiO_2-based photodetoxification products already on the market and a whole variety of self-cleaning and odor-destroying consumer products that utilize TiO_2 coatings are under development. Basic research on the photochemistry and photophysics of semiconductor particles such as TiO_2 has also led to improvements in the photostability of pigmented paints and in the production of photographic films.

Research on multi-electron catalysts is another area where solar hydrogen research has impacted related technologies. For example, scientists at Energy Conversion Devices, Inc. developed low-cost, non-precious metal electrocatalyst that are amorphous and highly disordered. These catalysts were developed for alkaline water electrolysis and fuel cells. However, these disordered materials also displayed utility for the reversible storage of hydrogen and were essential in the development and commercialization of the Ovonic nickel/metal hydride rechargeable battery technology.

Future research in the areas listed above can be expected to impact a variety of technologies. Research on the mechanisms of multi-electron processes may lead to improved catalysts for the water-gas shift reaction, hydrogenation reactions and other synthetic redox chemistries. In principle, systems like those described here for hydrogen production could be modified to allow for the use of

solar energy to drive other reactions such as CO_2 reduction (see report from panel B-1). Advances in photochemical hydrogen production technologies can be expected to undergo synergistic development with improvements in fuel cell and battery technologies for vehicles. Development of materials and structures used in photochemical processes has natural spin-off applications in areas such as photosensors, microelectronics and non-linear optical devices.

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PANEL B-3

PHOTODETOXIFICATION AND PURIFICATION OF WATER AND AIR

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Scope

The scope of interest in this section is basic research in photochemistry that can remove barriers to the development of photochemical technologies for the removal of hazardous chemicals from contaminated air or water (photodetoxification). Photochemistry is be broadly interpreted to include direct photochemistry, indirect photochemistry (sensitized and photocatalytic), photochemistry of species adsorbed on inert surfaces, and complementary effects of high energy radiation photons and particles. These may occur in either homogeneous or heterogeneous media. The photon source may span the range from ionizing radiation to the near infrared.

Present Status

Photochemical processes using sunlight or photons from artificial sources are in varying stages of development for use in the removal of hazardous substances from air or water. UV-hydrogen peroxide or ozone systems, for example, are commercially available for use in removal of organic compounds from contaminated groundwater. Systems based on the photocatalytic activity of titanium dioxide have been demonstrated on the pilot plant scale for removal of organic compounds from both air and water and small systems are commercially available. A wide range of other photochemistry has been investigated for use in correcting or preventing environmental contamination. Photocatalytic processes based on the use of semiconductors as the light absorber are the subject of a high level of interest at present since they have the potential to operate at mild conditions and can work without added reagents other than the oxygen in air or dissolved in the aqueous phase as an oxidizing agent. The methods being considered may produce carbon dioxide as the terminal product of the photochemistry or compounds in an intermediate state of oxidation that may be amenable to a subsequent treatment operation.

Barriers to Implementation

Implementation of photochemical processes requires that the photons be supplied at low cost and that they be used with the maximum efficiency for the removal of the target substances. The process cost will be determined by the cost of supplying the photons; the complexity of the system required to bring together the photons, the light absorber, target compound (if not the light absorber), and the oxidizing or other reagents that may be required; and the expenses related to keeping the system operating efficiently. The latter costs will include, replacement of lamps or solar collector materials as performance declines, replacement of consumable reagents, and regeneration or replacement of the photocatalyst when it is deactivated.

Many photochemical systems for decontaminating air and water will be expected to operate continuously and will use lamps that must efficiently convert electrical power into photon flux. To date the most efficient lamp is the low pressure mercury lamp in which electrical power is converted into a 254 nm photon flux at about 40% efficiency. The common fluorescent lamps emitting at longer wavelengths are low pressure mercury lamps coated on the inside with a phosphor which converts the 254 nm photons to less energetic visible photons that are transmitted by an inexpensive

glass envelope. Currently the lamp envelopes transmitting photons in the UV are made of fused quartz. This can make the lamps the single most expensive component of photochemical detoxification systems that require wavelengths below 300 nm.

Science to Remove Barriers

- Independent of the nature of the photochemistry in a photodetoxification process, it is critical that chemical and physical processes that reduce the efficiency of the conversion of target molecules be understood and eliminated or inhibited to the greatest extent possible. This requires a detailed understanding of the factors which determine whether the energy in excited states results in productive chemical transformations or is lost through radiative or thermal decay pathways to the ground state.

- Detailed understanding of the fundamental surface chemistry of the heterogeneous photocatalytic processes is required. This includes chemical transformations of adsorbed species and formation of intermediates that occur on the surfaces of illuminated semiconductors as well as the adsorption and desorption of reactants and products. When more than one target substance is present in the medium to be treated competitive as well as cooperative effects must be understood. Even for a stream with a single organic component competitive effects can arise since oxidation of all but the simplest compounds produces a sequence of intermediates along the path to carbon dioxide. The understanding of the photocatalytic process may benefit from studies which can compare reactions in homogeneous media, photo and thermal reactions on insulator surfaces, and photo and thermal reactions on semiconductor surfaces.

- In the case of aqueous photocatalytic systems, in order to understand the radical and redox chemistry occurring at surfaces more quantitative data is required for reaction rates on surfaces (including two-dimensional diffusion), adsorption and desorption kinetics of the molecular compounds and of radicals (at least of the long-lived radicals), and on the orientation of molecules and radicals on the catalyst surface (which may change significantly with pH in the case of charged species).

- Understanding of both the beneficial and undesirable interactions between photocatalysts and support materials is not available. The potential for participation of the support material in chemical transformations in photocatalytic systems is not well understood. The improvements that are achieved by modifications of semiconductors with metal or metal oxide deposits or substitution of metal ions into the host lattice are likewise not understood. Systematic improvement of photocatalysts requires that the chemical or physical phenomena responsible for changes in performance that arise from changes in catalyst formulation be understood. This may include identification of the nature of the active site or sites on semiconductor photocatalysts, and determination of factors which influence adsorption of target species.

- The pathways by which photocatalysts lose activity and methods for recovering activity need to be identified.

- Methods for synthesis of photocatalysts with controlled morphology and particle size and assembly of the catalyst system, which may include support and structure forming materials, need to be developed which take into account the requirements of efficient light harvesting, transport of chemical reactants to the surface and diffusion of products away from the surface.

- Fundamental understanding of the nature of the spectral transitions in glasses in the ultraviolet region from about 300 to 180 nm is required in order to develop lower cost lamps. The theory of spectral transitions in glasses and their dependence on bonding and the fundamental materials chemistry of UV transmitting silicate and non-silicate glasses need to be addressed. Success of this activity will impact the use of direct photochemistry for detoxification and the exploration of photocatalysts with band gaps greater than that of TiO_2 (3.0-3.2 eV). The latter includes photocatalysts with both energetic holes for oxidation and energetic electrons for reduction reactions.

Future Technologies

The understanding that basic research brings to the application of photochemistry to environmental concerns can also be applied to the development of technology for the synthesis of chemicals from simple feedstocks. It is thus complementary to work in the areas of photoelectrochemistry, photoconversion, carbon dioxide fixation, and hydrogen production. Selective response of substances to irradiation by light may also be applied to development of selective sensors.

New Areas of Photochemical Science with Intrinsic Importance and Significance for Energy Technology

Direct and indirect photochemical processes that use light in the solar spectrum or that can be operated using light from efficient light sources powered by electricity from renewable sources are required for the production of fuels and chemicals and for energy storage. They will also be important in the development of processes based on pollution prevention strategies and for correcting the problems caused by past practices which led to environmental contamination on a world wide scale. As the fundamental understanding for photochemical detoxification processes progresses it becomes more important that there be direct interaction between the scientists developing the chemistry and physics and the engineers that are developing the models and designs for reactors that embody the technology. This will insure that technology is implemented in the most efficient manner possible.

Impact of Basic Photochemical Science on Energy Technology Development

Basic research that has been done in organic photochemistry, inorganic photochemistry, radiation chemistry, and photoelectrochemistry provides the basis for the development of photochemical processes that can be applied to reversing environmental damage that has occurred in countries all over the world due to the inappropriate use and disposal of chemicals. This foundation also provides technologies that can be used to remove hazardous components from the air and water emissions of industrial processes, thus insuring that industrial activity does not repeat the errors of the past. In addition photochemical technologies under development can provide cleaner air for buildings and urban environments and clean drinking water for areas where it is not now available.

Addendum
Engineering and Application Barriers to Implementation of Photodetoxification

In order to complete the picture of the barriers to implementation of photochemical processes for environmental applications the panel felt that some of those in the more applied part of the R&D spectrum should be identified. Key technical issues in applied chemistry and engineering include:

- Innovation is required in the design of photochemical reactors. The problem of bringing light, one or more reactants, and a photocatalyst (if any) together in a cost effective way is key to implementation of photochemical technologies for use in chemical processes. Reactors will have unique design challenges depending on whether they use electric lamps or sunlight as the source of photons.

- Methods of modeling the processes that occur in photochemical reactors need to be developed so that reactors can be scaled up and performance predicted.

- Integration of photochemical processes into complete treatment systems that include other biological, physical, or chemical operations will require understanding of the optimum capabilities of each and design of control systems to make maximum use of the synergistic effects.

- Implementation of either direct or indirect photochemical processes for chemical destruction or synthesis will require optimization for each specific application that is considered.

- Environmental applications of photocatalytic chemistry for detoxification of air or water requires the development of new and more efficient catalysts (either homogeneous or heterogeneous). This can include, for example, wide band gap semiconductors for use with short wavelength UV (e.g. 254 nm), or systems analogous to the iron(+3)/oxalate/hydrogen peroxide homogeneous catalytic system (most effective below pH=3) that will work at pH >5.

- The implementation of solar processes for broad application in photodetoxification depends on development of indirect photochemistry that can use more of the solar spectrum than titanium dioxide.

- Successful implementation of photochemical processes for detoxification of air and water or for production of chemicals will require the work of scientists and engineers on problems which range from the very basic to questions of integration of process unit operations. This will require effective collaborations and exchange of information between teams of scientists and engineers.

PANEL C-1

BASIC MECHANISMS OF PHOTOSYNTHESIS AND APPLICATIONS TO IMPROVED PRODUCTION AND CONVERSION OF BIOMASS TO FUELS AND CHEMICAL PRODUCTS

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Natural photosynthesis, the result of 3.5 billion years of evolutionary experimentation, is the best proven, functional solar energy conversion technology. It is responsible for filling the vast majority of humanity's energy, nutritional, and materials needs. Understanding the basic physical chemical principles underlying photosynthesis as a working model system is vital to further exploitation of this natural technology. These principles can be used to improve or modify natural photosynthesis so that it is more efficient or so that it can produce unusual products such as hydrogen, methane, methanol, ethanol, diesel fuel substitutes, biodegradable materials, or other high value chemical products. Principles garnered from the natural process can also be used to design artificial photosynthetic devices that employ analogs of natural antenna and reaction center function, self-assembly and repair concepts, photoinduced charge transfer processes, photoprotection, and dark reactions that facilitate catalytic action to convert light into useful chemical or electrical energy.

The present broad understanding of many structural and functional aspects of photosynthesis has resulted from rapid recent research progress. X-ray structures of several key photosynthetic reaction centers and antenna systems are available, and the overall principles controlling photoinduced energy and electron transfer are being established. We can now begin to capitalize on this basic knowledge to unravel the remaining mysteries in the natural process, including the water-splitting process, and search for ways to use photosynthetic concepts to prepare new artificial and hybrid molecular systems that harvest energy and carry out useful functions.

We need to define very broadly new research directions that encompass any process whose energy efficiency can be improved by the use of light-driven charge separation and storage.

Critical current research opportunities in this field are identified as follows:

- The fundamental principles of photoinduced energy and charge transfer in natural and artificial photosystems need to be understood as functions of structure, energetics, and medium.

- The repertoire of donors and acceptors that optimize the fraction of captured photon energy needs to be expanded.

- There is a need to better define the energetics of charge separation and recombination reactions, which differ from those of charge shift reactions. For example, it is important to determine whether small reorganization energies are critical to efficient charge separation.

- The effect of the intervening medium between the donor and the acceptor on the electronic coupling between the donor and acceptor needs to be better understood. Can electronic barriers enhance the ratio of forward charge separation rates to recombination rates?

- It is important to determine the structures of transient intermediates in order to understand how to optimize charge separation efficiency. Can orientation or symmetry enhance charge

separation efficiency and lifetime? Can extended bonding in sigma or pi networks promote charge separation over very long distances?

- A fundamental understanding of the physics and chemistry of single photosystem photosynthesis (and its mimetic analogs) must be developed for the production of renewable fuels and chemicals. Coupling of simple stand-alone biological photosystems, such as Photosystem II, purple and green bacteria, as well as halobacteria, to fuel forming reactions should be carried out. Single natural photosystems can be used as design models for artificial systems.

- A deeper understanding of the diverse mechanisms involved in the antenna function in natural and artificial photosynthesis needs to be obtained in order to improve the efficiency and utility of artificial antenna systems. There needs to be a larger effort to produce artificial antenna systems. There are many natural antenna structures. What advantages do particular structures in nature have for energy collection, e.g., why do some antenna systems display a high degree of order as opposed to others which do not? Basic energy transfer mechanisms in antennae, such as exciton coherence, need to be addressed.

- Charge separation molecules that are fully functional in rigid media and in confined environments e.g., polymers, host-guest systems, and cage structures need to be investigated. In this context, the incorporation of structural features into artificial reaction centers that use their surroundings to promote vectorial electron transfer should be explored.

- Mechanisms of assembly of natural and artificial supramolecular light-utilizing systems need to be understood, if practical devices based on these systems are to be realized. As such, the assembly of photosynthetic proteins is poorly understood, as are strategies for self-assembly of redox components into a supramolecular photoconversion structures. The design and construction of hybrid systems using donor-acceptor systems along with synthetic peptides, polymers, nanocrystallites, and electrode surfaces should be researched in this context.

- The nature of the interaction of molecular and supramolecular assemblies with their surroundings e.g., anisotropic media and effects of solvent dynamics, should be probed. In this connection, the physical chemical properties of the protein as a solvent for photosynthetic charge separation should be investigated.

- Electron donor-acceptor systems and their photochemistry in anisotropic media e.g., liquid crystals, pulled and/or stretched polymers, should be explored in detail. "Synthetic solvents" that provide environmental control of electron transfer similar to that provided by photosynthetic proteins need to be prepared. The role of solvent dynamics on charge separation reactions needs to be explored in greater detail.

- Light driven, energy efficient, natural and artificial methods of charge accumulation for water splitting, and reduction of CO_2 and N_2 need to be developed. In this connection multi-redox

charge accumulators, analogous to the Oxygen Evolving Complex of the Photosystem II, need to be designed, prepared, and studied.

- The coupling of proton movement to charge transfer is common in natural photosynthetic systems. This strategy needs to be further explored in the development of artificial photosynthetic systems.

- The mechanisms of regulation, protection, and repair of artificial and natural photosynthetic systems needs to be better understood and exploited in artificial energy conversion systems. For example, it is important to learn how to incorporate photoprotective mechanisms into artificial photosynthetic molecules to prevent photodegradation. Can self-assembled systems repair themselves? How?

- Photoinduced charge transfer is at the core of many optical and electro-optical effects that have potential as information storage and processing techniques. The basic principles necessary to design and prepare energy efficient supramolecular systems naturally lead to molecular systems that possess desirable electronic and optoelectronic properties. These optical properties should be explored and exploited.

- Because nonlinear optical effects depend on charge polarization, they should be used as tools to develop a deeper understanding of charge separation. For example, photorefractive effects require charge separation over distances of several microns.

- Artificial photosynthetic molecules that use two sequential one-photon events within the same molecular system should be explored. Such reversible photoreactions may be used as optical switches to control other reactions. It may be possible to use electron transfer reactions to gate or control other processes using electric fields, proton translocation, photochromism, unusual redox states (e.g., Kok's "S" states of the Oxygen Evolving Complex), or light-induced conformational changes.

- The light-induced reactions must be appropriately coupled to secondary dark-reactions to perform useful chemical conversion processes such as fuels production, remediation, chemical detoxification, and chemical synthesis. In this context, studies of the dark reactions necessary for long-term storage and utilization of solar energy are needed, as well as, studies of the catalytic activity of the agents that promote the secondary reactions.

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