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FEATURE ARTICLE

Design of Semiconductor Photoelectrochemical Systems for Solar Energy Conversion

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The principles and applications of semiconductor electrodes in photoelectrochemical (PEC) cells for carrying out useful chemical reactions are described. The factors in the design of efficient and stable systems and semiconductor particulate systems constructed on the basis of PEC cell principles are discussed.

The efficient production of fuels from inexpensive precursors by utilization of solar energy with cheap and stable chemical systems has become the goal of numerous research efforts. Examples of desirable reactions are the reduction of water (or protons) to H_2 and the reduction of CO_2 to methanol driven by light. Because the effect of light in any system is the creation of electron–hole (e^-h^+) pairs, the fuel-producing reaction must be accompanied by an oxidation reaction. This oxidation reaction should consume an inexpensive or waste material (e.g., produce oxygen from water), or alternatively produce a substance of some value (e.g., Cl_2 from Cl^- oxidation). The model often used for such systems is biological photosynthesis, in which light is utilized to produce reduced (carbonaceous) materials and O_2. However, the field efficiencies of biological systems, in terms of conversions of solar energy to fuel value, is rarely better than 1% and the individual systems do not show long lives (but they are, of course, self-replicating). Man-made photosynthetic fuel-producing systems will have to show at least an order-of-magnitude better efficiency as well as lifetimes of many years.

A number of photochemical and thermochemical schemes have been proposed to effect such light-driven reactions. Among the most successful have been those involving the absorption of light and the occurrence of electron-transfer reactions at the semiconductor/liquid interface. The basic principles and examples of such liquid junction semiconductor devices have been the subject of a number of reviews.[1-5] I will emphasize in this paper the concepts involved in designing semiconductor photoelecltrochemical (PEC) systems, the recent research of our group, and some of the problems that still remain.

The general scheme for the construction of a photoelectrochemical system involving a single light absorber is shown in Figure 1. The energetics of the system, in terms of electron energy levels and redox potentials are given in Figure 2. In general, the overall reaction involves the following stages: (1) photon capture and e^-h^+ pair formation (1,2); (2) trapping of e^- and h^+ in rapid chemical reactions (3,5); and (3) Catalytic formation of final products (4,6) and separation. Light is captured in the light-absorbing system (1,2) which represents a support material and the sensitizer layer. This could be a metal substrate with a thin layer of semiconductor (e.g., TiO_2 on Ti), a transition metal complex, or an organic dye sensitizer on a semiconductor substrate (e.g., $Ru(bpy)_2^{2+}$ or ZnPc on TiO_2; where bpy is 2,2′-bipyridine and Pc is phthalocyanine). The light-absorbing system serves to convert the incident photons into electron–hole pairs and frequently provides a gradient in electrical or chemical potential to cause separation of e^- and h^+. Recombination of e^- and h^+ is also prevented if they are transferred rapidly to suitable acceptor, A(3), or donor, D(5), molecules. The couple represented by $A/A^-\cdot$ (e.g., MV^{2+}/MV^+ or S_x^{2-}/S^{2-}; where MV^{2+} is methyl viologen) should have as negative a redox potential as possible, consistent with rapid reaction with the photogenerated electron. It is unlikely that the fuel-producing reaction can occur directly at this stage, since these reactions frequently involve multielectron transfers and high-energy intermediates. Similarly the D/D^+ couple (e.g., Br^-/Br_2 or Fe^{2+}/Fe^{3+}) should be as positive as possible consistent with rapid reaction of the photogenerated h^+. The A/A^- and D/D^+ couples are sometimes called "relays", since they serve to transmit the photoproduced charges to the final desired electron-transfer reactions. As shown in Figure 2 formation of A^- and D^+ results in some degradation of the energy of the e^-h^+ pair. The spontaneous back-electron-transfer reaction between A^- and D^+ must be prevented by keeping them spacially separated or by having them react rapidly in a subsequent step. Similarly any reaction of A^- with h^+ or D^+ with e^- represents a loss in efficiency. The reaction of A^- to form fuel (e.g., $H^+ \rightarrow H_2$) usually will require a catalyst, CAT_R (4), which serves to couple the $A^- \rightarrow A$ and H^+ reduction reactions and provide a surface for adsorbed intermediates. Similarly an oxidation catalyst, CAT_O (6), will usually be required to couple the $D^+ \rightarrow D$ and the terminal oxidation (e.g., $H_2O \rightarrow O_2$) reaction. These catalyzed reactions again represent some degradation of the initial photon energy and again back-reactions (e.g., A^- or e^- with O_2) must be prevented. The total energy of the products, ΔG°_p, is less than the energy of the captured photon, given by the band gap of the light absorber, E_g, by the needed driving forces (or overpotentials) of the various electron-transfer steps. Thus if ΔG°_p is ~1.3 eV (representative of many fuel-forming reactions) and each electron-transfer step involves a ~0.2 eV overpotential, then E_g must be greater than 2.1 eV.

Principles of Semiconductor Electrodes

The principles of semiconductor electrodes as applied to photoelectrochemical cells have been discussed in a

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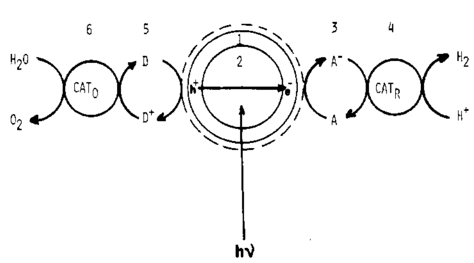

Figure 1. Schematic diagram of system for utilization of solar energy in a photoelectrosynthetic reaction (e.g., $H_2O \rightarrow H_2 + {}^1/_2O_2$). 1 and 2 represent the light-absorbing system and support; the dashed line around 1 and 2 represents a possible stabilizing layer on the system. 3 and 5 are redox couples, either in solution or incorporated onto the surface of the system; they act as the primary electron and hole acceptors. The final reaction is catalyzed by oxidation and reduction catalysts, CAT_O and CAT_R, respectively.

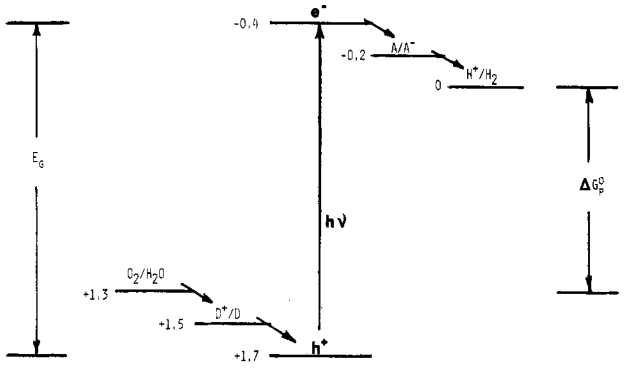

Figure 2. Representative energetics for the system in Figure 1. The numbers at the energy levels represent potentials in V vs. NHE for the reactions at pH 0. These potentials would shift by ~0.059 V per pH unit at 25 °C, so that, at pH 7, they would be about 0.4 V more negative.

number of reviews[1-7] and will only be outlined here. Basically a space charge layer forms at the semiconductor/liquid interface as the two phases come into electronic equilibrium (i.e., as the Fermi levels or electrochemical potentials become equal) (Figure 3). The electric field in this space charge region serves to separate the e^-h^+ pairs produced by light absorption. The direction of the field is usually such that holes move to the surface at n-type semiconductors and lead to oxidations while electrons move to the surface at p-type semiconductors and cause reductions. The primary energetics of the system can be obtained from a knowledge of the flat-band potential (which for highly doped semiconductors approximately corresponds to the location of the conduction band edge, E_c, in n-type semiconductors and the valence band edge, E_v, in p-type) and the band-gap energy, E_g. Typical values for n-TiO_2 and p-GaAs are shown in Figure 3. However, for a given semiconductor, the location of these energy levels depends upon the nature of the solvent, the presence of ions which adsorb on or react with the semiconductor surface, and the presence of surface states or surface charge which leads to nonideal behavior such as Fermi level pinning or inversion. However, at least as a first approximation, it is useful to consider that under irradiation holes and electrons are delivered at potentials corresponding to E_v and E_c, respectively. A PEC cell with a single absorbing semiconductor system and a metal or carbon counterelectrode thus can represent the general system of Figure 1 with e^-h^+ separation driven by the electric field in the space charge region and spacial separation of products preventing back-reaction.

Design of Semiconductor PEC Cells

The design of a practical photoelectrosynthetic cell (a PEC cell which converts radiant energy to chemical free energy) is based on both semiconductor and solution properties.

1. Band-Gap Energy. The value of E_g should be as small as possible consistent with driving the desired overall cell reaction. The maximum efficiency for terrestrial solar energy utilization occurs for E_g of 1.1–1.3 eV, although values up to ~2.0 eV can be used with reasonable efficiencies.[8]

2. Band-Edge Locations. The values of E_c and E_v, as represented by the corresponding redox levels, must be compatible with the desired half-reactions (A/A^- and D^+/D). The location of these levels depends not only on the inherent work function of the semiconductor but also upon the nature of the solvent and specific adsorption of ionic charge at the interface. The band-edge locations are frequently estimated from the flat-band potentials determined from plots of the interface capacitance with potential (Mott–Schottky plots) or, somewhat less reliably, from the potential for the onset of the photocurrent.

3. Stability. Both the thermodynamic and kinetic factors involved in stability of the semiconductor have been discussed.[9,10] The problem appears more acute with *n*-type materials where the photogenerated holes, which move to the interface, are capable of oxidizing the semiconductor itself. For example, with ZnO in an aqueous solution at pH 0 the half-reaction $ZnO + 2h^+ \rightarrow Zn^{2+} + {}^1/_2O_2$ ($E°_D$ = +0.9 V vs. NHE) can occur readily with holes produced at the potential of the valence band edge (~3.0 V vs. NHE). Thus irradiation of a ZnO electrode in an aqueous solution will cause at least partial decomposition of the semiconductor electrode. A number of approaches have been taken to stabilize the semiconductor. By proper choice of the D^+/D couple the photogenerated holes can be removed rapidly before decomposition can occur. If the standard potential of the D^+/D couple is more positive than $E°_D$, a direct attack by D^+ on the semiconductor is thermodynamically possible, however. It also appears that a thick layer of metal or conductive polymer on the electrode surface can serve to remove the photogenerated charge rapidly and stabilize the material.[11] If the solvent is changed to a nonaqueous one or the water activity is greatly decreased, $E°_D$ can be made more positive and the stability enhanced. Experiments are also under way on the modification of semiconductor surfaces, e.g., by derivatization or polymer-coating techniques, in attempts at improving stability.[12] For example, unprotected n-silicon in aqueous solutions forms an insulating oxide film under irradiation in aqueous solutions. However, when it is covered with a thin metal layer (Au or Pt) and a thicker polypyrrole film, it behaves as a stable photoanode in I^-/I_3^- and Fe^{2+}/Fe^{3+} solutions.[13] These films probably serve to

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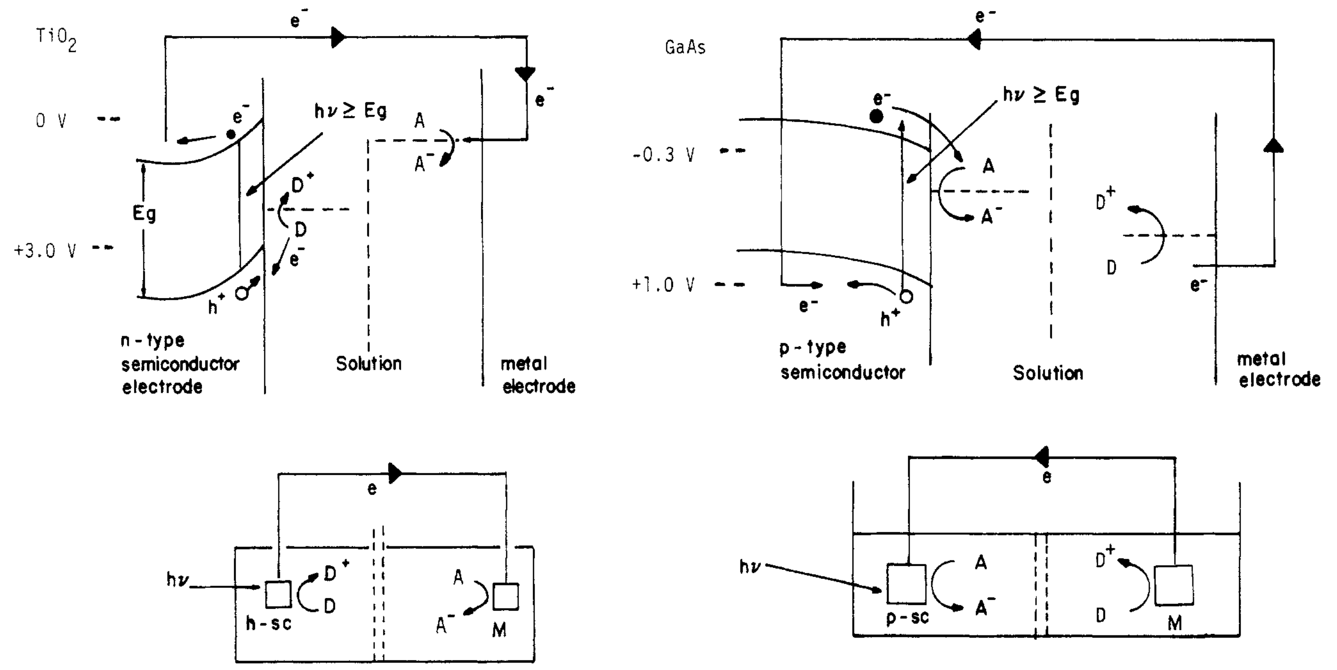

Figure 3. Schematic representation of (A) n-type semiconductor photoelectrochemical cells with typical values for the band-edge locations for n-TiO_2 at pH 0 (V vs. NHE). (B) p-type semiconductor cell with band-edge locations for p-GaAs at pH 0.

protect the semiconductor by removing the photogenerated h^+ and also by making the surface more hydrophobic. Some water penetration to the surface must still occur, however, since the addition of strong electrolyte (e.g., 11 M LiCl) to the solution to decrease water activity improves the stability even more.[13a] The technique of using high concentrations of electrolyte to decrease water activity while still providing a medium with high conductivity was used first by Wrighton et al.[14] to stabilize n-$MoSe_2$ during the photogeneration of chlorine in chloride media.

Although p-type materials can be reduced by the photogenerated electrons brought to the electrode surface (e.g., p-Cu_2O in aqueous electrolytes), in general they tend to be more stable in aqueous media than n-type and are, in fact, self-cathodically protected from oxidation.[15] The reduction of the p-type materials can also be suppressed by the use of nonaqueous media. For example, p-type Cu_2O can be employed in the reduction of nitrobenzene to its radical anion in acetonitrile.[16]

4. Doping Level. The thickness of the space charge layer and the resistance of the bulk semiconductor are controlled by the doping level. This can be adjusted so that the space charge layer extends sufficiently deep that essentially all of the incident light is absorbed within it. Higher doping of the bulk semiconductor is desirable, and n^+n or p^+p structures can be used to optimize efficiencies (where n^+ and p^+ refer to higher doping levels).

5. Crystallinity. From the standpoint of ease of production and low cost, polycrystalline semiconductor electrodes are needed. These have been prepared by a number of techniques (e.g., chemical vapor deposition, vacuum evaporation, sputtering, electrodeposition) and in many cases show efficiencies approaching those of single-crystal materials.

6. Surface Treatment. The nature of the semiconductor surface can be an important factor in the efficiency, since surface states can act as e^-h^+ recombination centers. Thus different etching, chemical pretreatment, and surface modification methods have been used to improve the cell performance. An example of this approach is the passivation of edges on n-WSe_2. Small single crystals of the layered compound WSe_2 show excellent photoelectrochemical efficiencies, when the surface is free from exposed edge planes. The presence of edges leads to significant dark oxidation currents and lower efficiencies. When these electrodes are employed to oxidize *o*-phenylenediamine, polymer formation occurs at the dark oxidation sites (presumably the edges), with greatly improved efficiencies in PEC cells.[17] Similarly selective adsorption of appropriate species (e.g., *tert*-butylpyridine) onto the edge planes can improve the performance of the layered compounds.[18]

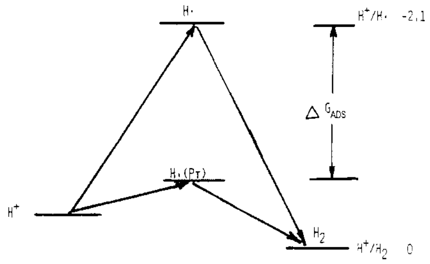

Figure 4. Representation of effect of Pt in catalysis of hydrogen evolution reaction. Potentials at pH 0 in V vs. NHE at right. ΔG_{ads} is the energy of adsorption of H atoms on Pt. The relative location of H^+ to H· and H_2 levels depends upon potential of the particle.

7. Redox Couple. The redox couples chosen for A/A^- and D/D^+ must satisfy a number of requirements. Both forms should be stable as well as highly soluble (>1 M) to prevent mass transport control of the current. The heterogeneous electron-transfer rates should be rapid and the redox potentials appropriate to drive the desired final fuel-producing reaction at the catalyst and yet be located where photodriven charge transfer and stabilization of the semiconductor occur. They should be inexpensive and neither form should absorb light of energy above E_g.

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Catalysis

Although the conduction band energy of several p-type electrodes (e.g., GaAs, Si) in aqueous electrolytes is at sufficiently negative values that direct reduction of protons to H_2 is thermodynamically possible, the hydrogen evolution reaction does not occur with good efficiency under illumination. This can be attributed to the slow reaction kinetics for hydrogen evolution at most electrode materials; in electrochemical terminology, most semiconductors show a high hydrogen overpotential. As depicted in Figure 4, formation of hydrogen atoms (H·) by the one-electron half-reaction requires a very negative potential. This energy can be overcome if H atoms are adsorbed as they are, for example, on Pt. The energy of adsorption of H· on most p-type semiconductors is apparently small. As was demonstrated with both p-GaAs[19] and p-Si,[20] the use of the rapid one-electron redox couple $MV^{2+}/MV^{+}\cdot$ and finely divided Pt promotes photogenerated hydrogen evolution. The Pt plays the role of a catalyst and allows the pooling of electrons so that the electron-transfer reactions $2H^+ + 2e^- \rightarrow H_2$ and $MV^{+}\cdot \rightarrow MV^{2+} + e^-$ can both occur at equal rates. An electrochemical model for this catalyzed electron transfer has recently been described.[21]

Direct oxygen evolution at semiconductors (e.g., n-TiO_2, n-Fe_2O_3, n-$SrTiO_3$) has been observed, but the valence band location in these is usually sufficiently positive that formation of the high-energy intermediate, hydroxyl radical (OH·) appears possible. Indeed, spin-trapping experiments demonstrate that at irradiated TiO_2 powders OH· is formed.[22] The production of O_2 utilizing an appropriate couple, D^+/D, and/or a heterogeneous catalyst should be possible. Improved rates of oxygen evolution with RuO_2 as a catalyst have been reported.[23] As discussed earlier, stability of small-band-gap semiconductors with appropriately placed valence band edges (e.g., at ~ +1.7 V vs. NHE at pH 0 or ~+1.3 V at pH 7) may be an important problem.

Other oxidation half-reactions, which are inherently more rapid and occur at less positive potentials, such as $2Br^- \rightarrow Br_2 + 2e^-$, may also be of interest. Another possibility is the use of "sacrificial" waste materials. For example, the photooxidation of acetate to produce ethane and CO_2 at n-TiO_2 occurs quite readily,[24] and acetate and other carboxylic acids are fermentation products obtainable from biomass. However, one should note that the overall reaction $2CH_3COOH \rightarrow C_2H_6 + CO_2 + H_2$ occurs with $\Delta G° < 0$, i.e., is thermodynamically downhill, so that the PEC cell reaction is really a photocatalytic (rather than an energy-storing photoelectrosynthetic) one.

Particulate Systems

The principles of semiconductor PEC cells can be applied to the design of particulate or powder systems for carrying out photoreactions.[1,2] For example, platinized TiO_2 powder in a rough sense can be visualized as a short-circuited photocell analogous to that of Figure 3. Light impinging on the TiO_2 again causes e^-h^+ pair formation and the Pt again appears to serve as an effective reduction site. While there have been few studies on the detailed mechanisms and physical-chemical nature of photoreactions at semiconductor powders in solution, a number of different photoreactions, including metal depositions, decarboxylations, polymerizations, and even small amounts of amino acid synthesis have been demonstrated.[1,2] Reduction of CO_2 to methanol and other reduced species on irradiated TiO_2, CdS, and GaP powders has also been reported,[25] although the overall efficiency for this reaction is quite low. Even the direct splitting of water to O_2 and H_2 has been accomplished with semiconductor/catalyst powders and colloids.[26] An electrochemical model can again be proposed for photoprocesses on semiconductor powders (Figure 5). However, the existence of a real space charge region in the small, usually lightly doped, particles is unlikely, and probably most charge separation occurs at the particle surface. Thus an alternative, more chemical way of looking at the photoprocess is as follows. Consider a TiO_2 particle. The e^-h^+ pair produced near the surface on irradiation forms, at least transiently, oxidized and reduced sites on the surface. Spin-trapping experiments[22] and the results of a number of photochemical studies (e.g., the formation of hydroxylated products during irradiation of benzene and benzoic acid) strongly indicate that the primary h^+-trapping step is formation of hydroxyl radicals.[27a] The nature of the reduced site is less certain. However, Ti(III) species in solution have been identified during irradiation of TiO_2 powders in the presence of oxalate ion,[27b] and this may represent the primary reduced species. The formation of a lattice $O_2^-\cdot$ species also appears possible from gas-phase studies of irradiated TiO_2[28] and spin-trapping[22] experiments. Thus the process can be written in chemical terms as

$$h\nu \rightarrow h^+ + e^-$$

$$\cdots OH^- + h^+ \rightarrow \cdots OH\cdot \qquad \text{(primary oxidation step)}$$

$$Ti(IV)O_2 + e^- \rightarrow Ti(III)\cdots O_2 \text{ or } Ti(IV)\cdots O_2^-\cdot \qquad \text{(primary reduction step)}$$

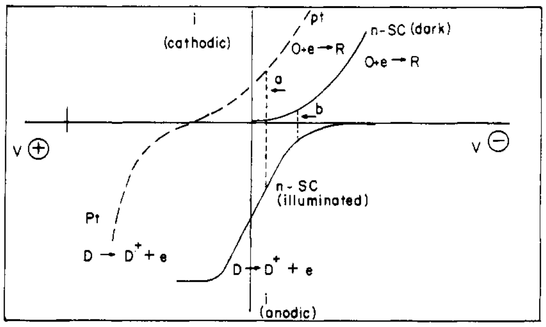

Figure 5. The application of individual electrode (semiconductor and Pt) current–potential ($i-V$) curves in the design of photoelectrochemical cells and particulate systems. Curves shown are for an n-type semiconductor (e.g., n-TiO_2) as shown in Figure 3A. The broken lines show the behavior for the oxidation ($D \rightarrow D^+$) and reduction ($O \rightarrow R$, e.g., H_2 evolution) at Pt and the solid lines at the irradiated semiconductor. The $D \rightarrow D^+$ reaction occurs at less positive potentials at the semiconductor because it is driven by light. a is the operating point for a semiconductor/Pt system and b is for the semiconductor alone. The higher currents at the operating point show that the platinized semiconductor should show a high reaction rate.

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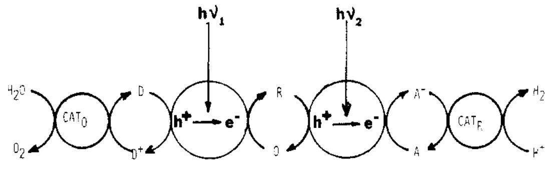

Figure 6. Schematic diagram of a solar energy utilization system employing two light absorbers and requiring two photons (at energies $h\nu_1$ and $h\nu_2$) to drive one electron through the system. The system is similar to that in Figure 1, except that an intermediate redox couple, O/R, connects the two light-absorbing systems.

Subsequent reactions of the oxidized and reduced forms lead to recombination or to the final products. Surface catalysts can promote these secondary reactions, e.g.

$$\mathrm{Ti(III)\cdots O_2} + \mathrm{H}^+ \xrightarrow{\mathrm{Pt}} \mathrm{Ti(IV)\cdots O_2} + {}^1/_2\mathrm{H_2}$$

The powder systems are of interest because they are inexpensive and relatively easy to fabricate. However, they do not offer the large spatial separation of the initially produced oxidized and reduced forms of the PEC cells and the final products from particulate systems are formed as a mixture rather than in separate streams. There are numerous studies of photoreactions at powders underway and new physical methods of characterizing the photoprocesses in solution (e.g., photoelectrophoretic,[29] electrochemical,[29] conductance,[30] and flash photolysis[26b]), as well as powerful microscopic and spectroscopic methods of examining the powders under vacuum, are emerging.

The State-of-the-Art and the Future

The solar power efficiency of most photoelectrosynthetic systems with no input of external electrical energy is generally about 1-2% in terms of fuel value of products out vs. solar energy in. Photoassisted processes, where an electrical bias is applied to the PEC cell and both radiant and electrical energy are used to produce products, show higher efficiencies but are of less interest from a practical viewpoint. These photoelectrosynthetic efficiencies are 5-10 times smaller than those obtainable with liquid junction photovoltaic cells. Improvements in performance and practical cell construction require consideration of the following:

1. *Energetics.* As discussed in the introduction, consideration of the driving forces needed to carry out a fuel-producing reaction suggest that an $E_g \geq 2.1$ eV is required. This value is outside the range of maximum efficiency of solar energy utilization and can be contrasted to the smaller band-gap materials used in photovoltaic cells (e.g., GaAs and InP; $E_g = \sim 1.3$ eV) where output voltage (usually < 0.6 V) is not a major factor. A suggested approach to the more effective utilization of solar energy is a dual light-absorbing system,[1] depicted in Figure 6. In this case the needed energy can be obtained from two small band-gap semiconductors ($E_g \sim 1.3$ eV) (Figure 7). While two photons are now required in this system to drive a single electron through the redox chain, the smaller band gaps allow a much better match to the solar spectrum. The light-absorbing systems could be two n-, two p-, or an n- and p-type semiconductor utilizing the O/R redox pair to couple to the two systems. An alternative approach is the use of n- and p-type materials connected with an ohmic junction ("photochemical diodes") to couple two photons into the overall chemical reaction.[31]

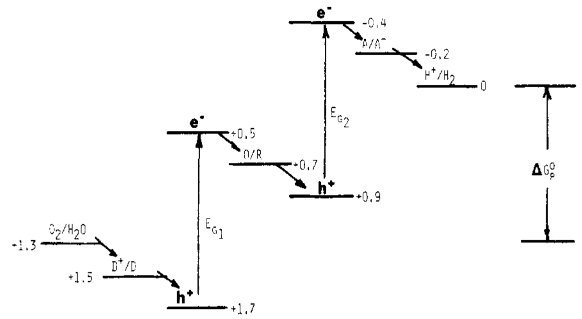

Figure 7. Representative energetics for the system in Figure 6. See Figure 2 caption for other information.

In particulate systems involving such dual light absorbers, special pains will have to be taken to avoid "short-circuiting" reactions of the intermediate redox species from greatly reducing the efficiency. One approach may be the immobilization of some of the redox couples on the surfaces within polymer layers.

An important apparent problem in the energetic analysis described above is the existence of "Fermi level pinning".[32] Briefly, it appears that surface states within the semiconductor band gap, if present at a sufficiently high density, can pin the Fermi level in the semiconductor at a value that is less than the total gap energy. For example, with both p-Si and p-GaAs maximum photovoltages of only ~0.6 V are obtained in liquid junction photocells. This would imply that larger band-gap materials may be required to drive the desired reactions. A positive aspect of Fermi level pinning is that the semiconductor band edges can be moved with respect to solution redox energy levels to carry out reactions which would not appear possible by consideration only of the semiconductor electrode energetics in the solution in the absence of redox couples. Surface treatment to decrease the extent of Fermi level pinning may be possible.

2. *Kinetics.* Recombination of the initially formed e^-h^+ pair, as well as intermediates on particulate systems, decreases the efficiency. The extent of recombination can be decreased by improving the kinetics of removal of e^- and h^+ to form final products. There is some evidence that surface states and grain boundaries can act as recombination centers and methods of passivating these by specific chemical treatment have been proposed.[33]

3. *Stability.* A key problem appears to be stability of the small band-gap semiconductors to the reactive intermediates, e.g., those in the oxygen-evolution reaction, or to the very positive redox couples (D^+/D) needed to drive the oxidation. Various approaches, such as covering the surface with a passivating or polymer layer or employing surface modification are under investigation. The rapid removal of photogenerated charge and reactive intermediates by use of a catalyst on the electrode surface also promotes semiconductor stability. Another approach involves the use of larger band-gap and stable semiconductors, e.g., TiO_2, and a sensitizer layer (e.g., an organic dye, $Ru(bpy)_3{}^{2+}$,[34-36] metal phthalocyanine[37]) to allow the uti-

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lization of lower energy radiation. A number of examples of sensitized processes at semiconductors have been described, but so far the observed efficiencies have been rather low because thin sensitizer layers do not absorb sufficient quantities of light and thicker layers tend to be resistive. In some cases, recombination processes within the sensitizer layers and dye stability also appear to be problems. However, this approach, particularly with particle systems, is still under active investigation.[23,38]

Conclusions

About a decade has passed since Honda and Fujishima[39] suggested that PEC cells based on single-crystal n-type TiO_2 might be used for the photodecomposition of water to H_2 and O_2. During this period much has been established about the behavior of the semiconductor/liquid interface and many new materials have been investigated. Particulate systems have been devised and a number of different photocatalytic and photoelectrosynthetic methods have been developed. While the goal of an efficient and stable system for the direct solar production of fuels remains an elusive one, semiconductor-based systems remain the most efficient chemical systems described so far for such reactions. Moreover, research in photoelectrochemistry has led to an improved understanding of the semiconductor/liquid interface and the photoprocesses which occur there. It has also provided new insight into a variety of processes (electrochemical, photographic, catalytic, photolytic).

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ARTICLES

Excitation Energy Dependence of the Phosphorescence to Fluorescence Quantum Yield Ratio of $NaNO_2$ Crystal. An Interplay between the Energy-Dependent Intersystem Crossing and Vibrational Relaxation

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The fluorescence and the phosphorescence of neat $NaNO_2$ crystal is observed at 4.2 K. The potential energy surfaces of the $^1B_1(n\pi^*)$ and $^3B_1(n\pi^*)$ states are determined on the basis of the vibronic structures. The O–N–O bond angle differs from that of the ground state by 9.6° for $^1B_1(n\pi^*)$ and 8.7° for $^3B_1(n\pi^*)$. The N–O bond length differs by 0.05 Å for either state. The excitation energy dependence of the phosphorescence to fluorescence quantum yield ratios (ϕ_P/ϕ_F) are determined at various excitation energies between $\sim$26 000 cm^{-1} and $\sim$34 000 cm^{-1}. As the excitation energy increases, the ϕ_P/ϕ_F ratio increases. Especially, a remarkable increase at $\sim$28 000 cm^{-1} is noted. It is shown that none of the previously suggested mechanisms account for the sharp increase of the ϕ_P/ϕ_F ratio at excitation energy as low as $\sim$28 000 cm^{-1}. From a model calculation we conclude that this excitation energy dependence of the ϕ_P/ϕ_F ratio is ascribed to an interplay between the energy-dependent intersystem crossing and vibrational relaxation.

1. Introduction

The quantum yield of the $^1B_1(n\pi^*) \rightarrow {}^1A_1$ fluorescence[1] and the $^3B_1(n\pi^*) \rightarrow {}^1A_1$ phosphorescence[2] of NO_2^- (the x axis being perpendicular to the O–N–O plane) has been shown to depend on the excitation energy.[1,3-5] It is now understood that this excitation energy dependence of the quantum yield is due to the fact that the rate of the intersystem crossing from the highly excited (vibronic or electronic) singlet state to triplet states depends on the energy of the initially prepared singlet state. As to the mechanism of this energy-dependent intersystem crossing, however, a variety of interpretations have been given previously, and it appears that no unambiguous interpretation has yet been established.

In 1962 Makishima et al.[1] reported that the fluorescence quantum yield of $NaNO_2$ crystal decreases when excitation is carried out to higher vibrational levels of the first excited singlet state, $^1B_1(n\pi^*)$. Similar observation was also reported by Rebane, Avarmaa, and Rebane[3] for NO_2^- in alkali halide (KCl, KBr, and KI) hosts. This observation indicates the existence of an energy-dependent nonradia-

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