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Photoelectrochemical Conversion of Optical Energy to Electricity and Fuels

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Though the first documented[1] photovoltaic effect is associated with a semiconductor/liquid junction, it has not been until very recently that significant solar energy conversion efficiency could be realized with a photoelectrochemical device. A semiconductor/liquid junction solar cell is one in which one or both electrodes is a semiconductor such that irradiation of the semiconductor(s) results in the nonspontaneous flow of electric current in the external circuit. Photogeneration of storable chemical fuels in the form of electrolytic products is possible, in addition to the prospect of converting light only to electricity when the redox reaction occurring at one electrode is the reverse of that at the other. The aim of this Account is to outline our recent research accomplishments in the field of photoelectrochemistry. Our work in this area began in late 1974—more than a century after the first studies[1] of photoeffects upon irradiation of an electrode in a cell and a number of years after modern pioneering studies of semiconductor/liquid interfaces[2-5] which led to the formulation of our present working hypotheses of such interfaces exposed to optical illumination.

Our research in semiconductor photoelectrochemistry began when a good working model for the semiconductor/liquid junction had already been formulated and perhaps best articulated by Heinz Gerischer.[6a] A summary of the junction characteristics is essential to an appreciation of the problems confronting us when we began. We briefly describe the interfacial situation essentially in Gerischer's terms.

Immersion of a semiconductor electrode into a liquid electrolyte solution may result in charge-transfer equilibration between the two media. The potential of the electrode, E_f, is then poised to the electrochemical potential of the solution, E_{redox}. The interesting finding is that the equilibration results in a relatively thick space-charge layer in the semiconductor near the surface exposed to the liquid. For semiconductors where the majority charge carriers are positive holes, the material is referred to as p-type, and where the majority charge carriers are negative electrons, the material is referred to as n-type. The effect of the equilibration is to reduce the majority charge carrier density near the surface, and the space-charge layer is therefore also referred to as the depletion region. Scheme I shows the interface energetics for n- and p-type semiconductors immersed in liquid electrolyte solutions. E_{VB} denotes the top of the valence band and can be regarded as the position of the highest occupied molecular orbitals delocalized over the solid, and E_{CB} denotes the bottom of the conduction band which represents the lowest unoccupied molecular orbitals. The energetic separation of E_{VB} and E_{CB} is the band gap, E_{BG}, and light of energy $\geq E_{BG}$ is useful in exciting electrons from the valence band to the conduction band. The objective in energy conversion applications is to efficiently transduce the excited electron hole pairs to produce electricity or chemical fuel. In Scheme I, the depletion region is that region in the semiconductor near the interface where the bands are bent, upward for the n-type and downward for the p-type semiconductor.

For a given semiconductor/liquid junction the positions E_{VB} and E_{CB} are generally taken to be fixed relative to E_{redox}. Owing to the band bending, photogenerated minority carriers (e^-'s for p-type, holes for n-type) are driven to the surface exposed to the liquid and are available for redox reaction. The hole for n-type materials has an oxidizing power no greater than E_{VB}, while the e^-'s for a p-type photocathode have a reducing power equal to E_{CB}. However, just what redox processes can be light driven depends on interfacial charge-transfer kinetics (vide infra). Scheme II summarizes the interface energetics and circuits for so-called

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(1) Becquerel, E. *C. R. Hebd. Seances Acad. Sci.* **1839**, *9*, 561.
(2) Gerischer, H. In "Physical Chemistry: An Advanced Treatise"; Eyring, H.; Henderson, D.; and Jost, W. Eds.; Academic Press: New York, 1970; Vol. 9A, Chapter 5.
(3) Myamlin, V. A.; Pleskov, Yu. V. "Electrochemistry of Semiconductors"; Plenum: New York, 1967.
(4) (a) Brattain, W. H.; Garrett, C. G. B. *Bell System Tech. J* **1955**, *34*, 129. (b) Dewald, J. F. In "Semiconductors"; N. B. Hannay, Ed.; Reinhold: New York, 1960; pp 727–752.
(5) Williams, R. *J. Chem. Phys.* **1960**, *32*, 1505.
(6) (a) Gerischer, H. *J. Electroanal. Chem.* **1975**, *68*, 263. (b) Bolts, J. M.; Ellis, A. B.; Legg, K. D.; Wrighton, M. S. *J. Am. Chem. Soc.* **1977**, *99*, 4826.

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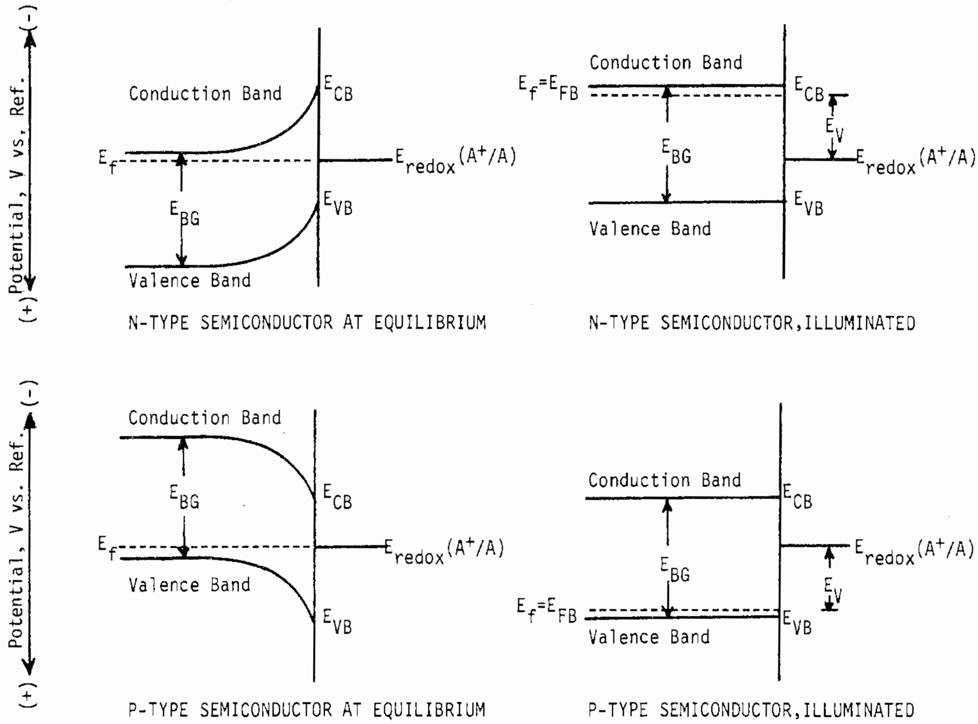
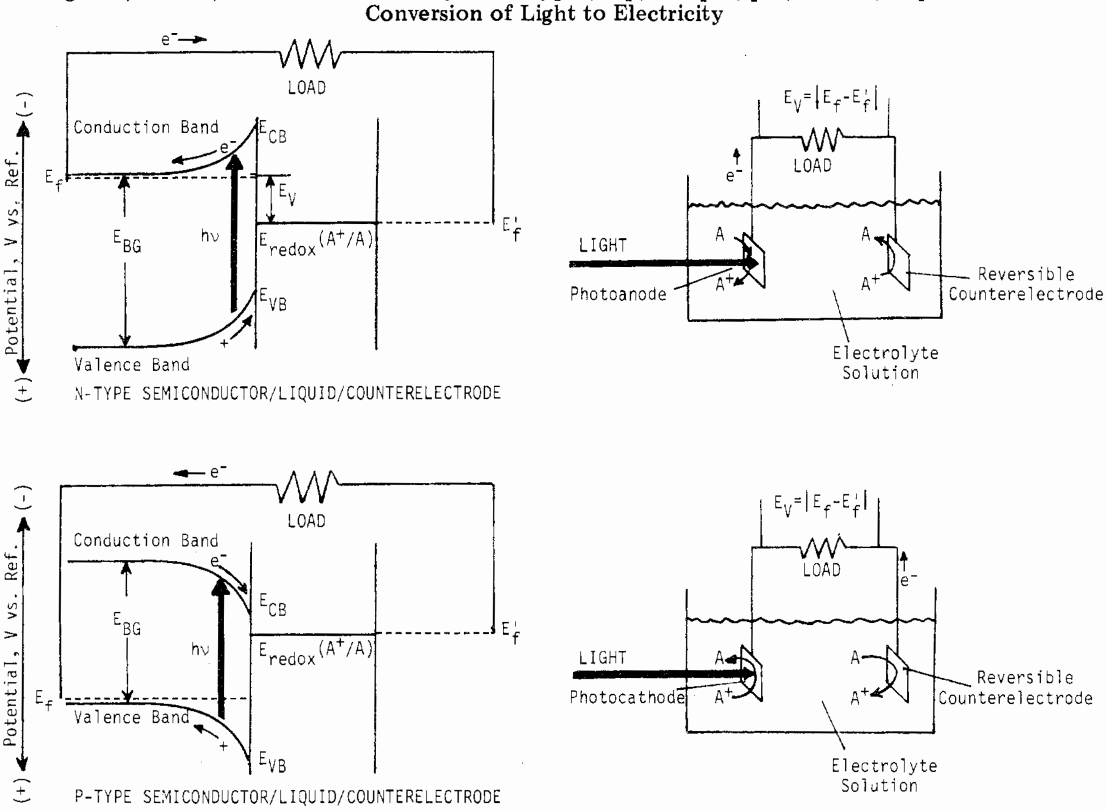
Scheme I
Semiconductor/Liquid Junction Energetics for an n-Type Semiconductor (Top) and a p-Type Semiconductor (Bottom) at Charge Transfer Equilibrium (Left) and under Illumination at Open Circuit (Right)[a]



[a] E_{redox} denotes the Fermi level of the liquid and E_f the Fermi level of the semiconductor. E_{FB} is the so-called flat-band potential where the bands are not bent.

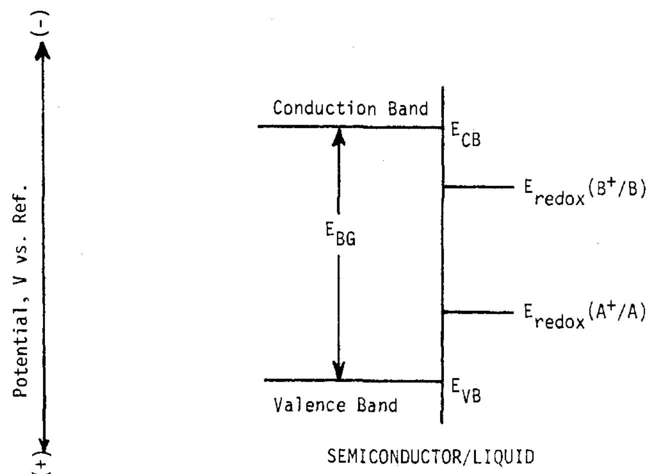
Scheme II
Full Cell Energetics, Circuit, and Redox Chemistry for n-Type (Top) and p-Type (Bottom) Liquid Junction Cells for Conversion of Light to Electricity



regenerative cells, where the reaction occurring at the photoelectrode is the reverse of that at the counterelectrode. The objective is to optimize the product of output voltage, E_V, and photocurrent. Increased band bending reduces E_V but inhibits electron–hole recombination and back-reaction. Approximately 0.3 V of band bending is needed to give quantum yields for electron flow approaching unity.

When fuel formation in the form of electrolytic products is desired, the reaction at the photoelectrode

Scheme III
Energetics Required To Be Able to Photochemically Drive the Reduction of B^+ *and* the Oxidation of A with No Other Energy Input Than Light



is not simply the reverse of that at the counterelectrode. For example, photoelectrolysis of H_2O involves the H_2O/H_2 couple at one electrode and the O_2/H_2O couple at the other. The desired energetic situation is that the E_{CB} and E_{VB} positions straddle the potentials of the solution couples (Scheme III) so that the excited electron–hole pairs have the oxidizing and reducing power needed to drive the two half-cell reactions. In such a case, no energy input other than light is needed to produce the fuel.

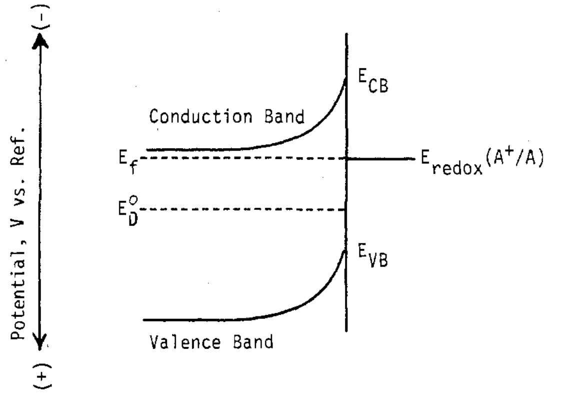
The Practical Problems

Unfortunately, anodic reaction of n-type semiconductors is a hole process competitive with other hole processes, and in particular, photoanodic decomposition competes with the oxidation of solution reductants. *The consequence of photoanodic reaction of the semiconductor is disaster: the photoelectrode is either irreversibly consumed or surface corroded in a manner which renders it useless.* All n-type semiconductors are subject to photoanodic decomposition, since the formal potential for oxidative decomposition, $E_D°$, is more negative than E_{VB}.[7,8] Further, if $E_{redox}(A^+/A)$ is more positive than $E_D°$, spontaneous oxidation of the semiconductor by the electrolyte solution is possible in the dark. The rates of the various hole processes determine whether a given system will be inert; as always, thermodynamics reveals only what is possible, not the rate of a spontaneous process. But it is an empirical fact that all non-oxide n-type semiconductors undergo photoanodic decomposition reaction in aqueous electrolytes. Even some very thermodynamically robust oxides are susceptible to photoanodic decomposition; the oxidizing power of photogenerated holes in such materials can be greater than that of elemental fluorine.

Incorporating the notion that anodic decomposition can occur results in limitations to what junctions are thermodynamically stable. Further, to the extent that $E_D°$ is above E_{VB} one cannot obtain a thermodynamically stable junction having a barrier height equal to E_{BG}, suggesting that efficiency will be limited to a value somewhat below theoretical.[7] Scheme IV shows a

(7) Bard, A. J.; Wrighton, M. S. *J. Electrochem. Soc.* **1977**, *124*, 1706.
(8) (a) Gerischer, H. *J. Electroanal. Chem.* **1977**, *82*, 133. (b) Gerischer, H.; Mindt, W. *Electrochim. Acta* **1968**, *13*, 1329.

Scheme IV
Interface Energetics for a Semiconductor/Liquid Junction Which Is Thermodynamically Stable to Oxidative Decomposition of the Semiconductor[a]



[a] The semiconductor decomposition potential, $E_D°$, is more positive than the solution potential, $E_{redox}(A^+/A)$.

thermodynamically stable junction with respect to oxidative processes, but whether the semiconductor is observed to be durable under illumination depends on the $A \rightarrow A^+$ conversion having 100% current efficiency; that is, the rate of oxidation of A by the photogenerated hole must be infinitely greater than the rate of oxidative decomposition of the semiconductor. The sustained operation of a semiconductor/liquid junction cell, therefore, depends crucially on the kinetics of interfacial charge transfer. It has been speculated that *all* p-type materials undergo decomposition at least on the surface, simply upon immersion into an electrolyte solution, since the value of E_f at E_{FB} is near E_{VB} and there are holes available in the dark to provide a mechanism for oxidation.[7] Also, photocathodic decomposition of p-type materials may limit their use.[7,8]

While maintaining the integrity of the photosensitive electrode surface is essential to any sustained energy conversion, the conversion *efficiency* will depend on the quantum yield, E_V, and the match of E_{BG} to the optical energy source. Like all other photovoltaic devices, the semiconductor/liquid junction cell is a threshold response system: light $< E_{BG}$ in energy is completely transmitted and therefore ineffective, but light $> E_{BG}$ is no more effective than light of energy E_{BG}. Sunlight is polychromatic, and the theoretical solar energy conversion efficiency maximizes at about 30% for a single photoelectrode-based cell with an optimum E_{BG} of $\sim$1.4 eV;[9] a double photoelectrode (p-type photocathode, n-type photoanode)[6b] cell with two different band gaps could ideally be over 40% in efficiency![9]

Photoelectrolysis of Water

In 1972, Fujishima and Honda reported the sustained oxidation of H_2O at illuminated TiO_2.[10] Their paper, frustration at gasoline stations, and the desire to gain funding and entry in a new research field stimulated us to begin our work in photoelectrochemistry. Early in 1975 we published the results of an investigation concerning the use of n-type TiO_2 as a photoanode in a cell for the photoelectrolysis of H_2O to H_2 and O_2.[11] Experiments were carried out in $H_2O/D_2{}^{18}O$ solution,

(9) "Solar Photovoltaic Energy Conversion"; The American Physical Society: New York, 1979.
(10) Fujishima, A.; Honda, K. *Nature (London)* **1972**, *238*, 37.
(11) Wrighton, M. S.; Ginley, D. S.; Wolczanski, P. T.; Ellis, A. B.; Morse, D. L.; Lintz, A. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 1518.

and gases evolved at photoanode (TiO_2) and cathode (Pt) were identified as $^{18}O^{16}O$, $^{16}O_2$, $^{18}O_2$ and H_2, HD, and D_2 by mass spectroscopy. Current efficiencies for the production of O_2 and H_2 were essentially in accord with eq 1 and 2, and measurement of the mass of TiO_2

[photoanode]

$$H_2O \xrightarrow{2h^+ (2h\nu)} 0.5O_2 + 2H^+ + (TiO_2) \quad (1)$$

[counterelectrode]

$$2H^+ \xrightarrow{2e^-} H_2 \text{ (Pt)} \quad (2)$$

before and after prolonged photoelectrolysis was the same. Finally, current densities of ~0.5 A/cm² for O_2 evolution were sustained in alkaline solution, using UV-laser excitation for H_2O oxidation. These data provided compelling proof that TiO_2 is a very durable photoanode material for the highest sustained rate of optical to chemical energy conversion ever demonstrated.

But additionally, we found that the chemistry represented in eq 1 and 2 could not be effected by simply short-circuiting TiO_2 to Pt and illuminating with $>E_{BG}$ = 3.0-eV light. Rather, it was found that a power supply in series in the external circuit providing ~0.2 V of driving force is needed. The value of E_V for O_2 evolution is only ~1.0 V. Thus, though the water splitting requires a potential difference of only 1.23 eV, the 3.0-eV band gap TiO_2 could not achieve this minimum voltage. The difficulty is readily appreciated from the fact that the TiO_2 band positions relative to the H_2 and O_2 evolution potentials are such that E_{CB} is more positive than the H_2 evolution potential by ~0.2 V. Clearly, the photogenerated hole is capable (thermodynamically) of oxidizing H_2O to O_2, but the excited electron potential is not more negative than E_{CB} and falls shy of the H_2 evolution potential by the ~0.2 V needed from the power supply. It is very likely that short-circuit photocurrents observed in TiO_2-based cells in fact correspond to H_2O oxidation to O_2 but do not involve H_2 evolution at the Pt; rather, the cathode reaction is reduction of O_2 or some other electrolyte impurity. Indeed, Bard[12] has exploited the TiO_2 system to generate electricity: $H_2O \rightarrow O_2$ (photoanode); $O_2 \rightarrow H_2O$ (cathode). Such a cell is inefficient for solar conversion owing to the large E_{BG} of TiO_2 which results in only ultraviolet response.

TiO_2-based cells as practical systems suffer from too large a band gap and the need for the external driving force in series with the photoeffect. The ideal photoelectrode would have the interface energetics as sketched in Scheme III where the O_2 and H_2 evolution potentials are the solution potentials of importance. Valence band holes would effect O_2 evolution, and conduction band electrons would have the potential to evolve H_2. Excess energy in the E_{BG} compared to the 1.23 V needed to split H_2O would be necessary to drive the redox chemistry at a fast rate.

In 1976 we,[13] and independently two other groups,[14,15] reported the first sustained conversion of H_2O stoichiometrically to H_2 and O_2, using light as the only input energy source, employing an n-type $SrTiO_3$-based cell. For $SrTiO_3$ the short-circuit, full cell energetics are such that E_{CB} and E_{VB} straddle the H_2 and O_2 evolution potentials. Like TiO_2, $SrTiO_3$ is a very durable material and was found to remain unchanged after prolonged use as a photoanode in alkaline media.[13] Unfortunately, $SrTiO_3$ has too large a band gap to be useful in solar energy applications, but such a cell has monochromatic ultraviolet light to stored chemical energy conversion efficiency in the range of 25–30%! This still represents the state of the science in photoelectrolysis, with a solar energy conversion efficiency in the range of 1%.

$SrTiO_3$-based cells have also been used to demonstrate the highest sustained rate of optical to chemical energy.[16] With an Ar ion laser tuned to the 351, 364 nm doublet emission, we showed that the photoelectrolysis of H_2O can be effected with an O_2 evolution current density exceeding 5 A/cm². The efficiency of the energy conversion was determined to be largely independent of the energy conversion rate. The data showed $SrTiO_3$-based cells to be able to generate >30 W/cm² of stored chemical energy in the form of H_2 and O_2 without substantial decline in efficiency, and there was no detectable deterioration of the photoanode material.

Platinized single-crystal n-type semiconducting $SrTiO_3$ effects the evolution of *both* H_2 and O_2 from H_2O when illuminated with ultraviolet light in aqueous electrolyte solutions.[17] The results are not surprising in view of the interface energetics; platinizing the $SrTiO_3$ surface is not unlike short-circuiting the semiconductor to a Pt counterelectrode. For the platinized material O_2 is evolved at illuminated, naked $SrTiO_3$ whereas the platinized portions serve as the cathode (site of H_2 evolution). Such platinized semiconductor material can be no more efficient than the electrochemical cell and suffers the disadvantages of (1) nonuseful light absorption by the Pt, (2) evolution of H_2 and O_2 in the same region of space, and (3) inability to run the photoelectrolysis at the "maximum power

Table I
Durable Photoanode Materials for Photoelectrolysis of Water[a]

material	E_{BG}, eV	comments	ref
TiO_2	3.0	rugged, but E_{BG} too large and E_{CB} and E_{VB} too positive	11, 16
$SrTiO_3$	3.2	basis of most efficient cell for H_2, O_2 production, E_{BG} too large, E_{VB} too positive	13, 16, 17
SnO_2	3.5	E_{BG} too large; E_{CB} and E_{VB} too positive; produces H_2O_2 in acidic media	16, 18a
$KTaO_3$	3.4	E_{BG} too large, E_{VB} too positive	18b
Fe_2O_3	~2.2	relatively good visible response, but E_{VB} and E_{CB} too positive	19

[a] Many other "stable" photoanodes are known (see ref 19); these are representative.

(12) Laser, D.; Bard, A. J. *J. Electrochem. Soc.* **1975**, *123*, 1027.
(13) Wrighton, M. S.; Ellis, A. B.; Wolczanski, P. T.; Morse, D. L.; Abrahamson, H. B.; Ginley, D. S. *J. Am. Chem. Soc.* **1976**, *98*, 2774.
(14) Watanabe, T.; Fujishima, A.; Honda, K. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 355.
(15) Mavroides, J. G.; Kafalas, J. A.; Kolesar, D. F. *Appl. Phys. Lett.* **1976**, *28*, 241.
(16) (a) Wrighton, M. S.; Bocarsly, A. B.; Bolts, J. M. *Prog. Astronaut. Aeronaut.* **1978**, *61*, 613. (b) Bocarsly, A. B.; Bolts, J. M.; Cummins, P. G.; Wrighton, M. S. *Appl. Phys. Lett.* **1977**, *31*, 568.
(17) Wrighton, M. S.; Wolczanski, P. T.; Ellis, A. B. *J. Solid State Chem.* **1977**, *22*, 17.

point" of the photocurrent/potential curve associated with the photoelectrolysis of H_2O.

There have been a number of other n-type semiconducting oxides used as the photoanode in a cell for the electrolysis of H_2O. So far, all materials used suffer from at least one of the following: poor wavelength response, decomposition, or improper disposition of the band edges relative to the H_2 and O_2 evolution potentials[18,19] (Table I).

The improper disposition of bands is a difficulty which at first would seem surmountable by simply varying the pH at which the photoelectrolysis is conducted. The rationale is that both O_2 and H_2 evolution are pH sensitive but always separated by a minimum of 1.23 V. The idea is that if the conduction band falls shy of the H_2 evolution potential then the pH could be lowered to move the H_2 evolution to a more positive value. For semiconductors generally, this may be possible, but for the oxides studied thus far they are either soluble at a useful pH or the E_{CB} and E_{VB} positions move with pH such that E_{CB} and E_{VB} and O_2 and H_2 are all constant relative to each other.[20] The pH dependence of the band edges is a consequence of surface acid–base equilibria resulting in a different chemical composition at the surface as the pH is varied. Generally, E_{VB} and E_{CB} will only remain fixed if the solution has a constant composition.

Non-Oxide, n-Type Semiconductors and Electricity Generation

There is not a single non-oxide, n-type semiconductor which has been shown to be capable of sustaining O_2 evolution from H_2O when illuminated. Rather, all such materials undergo efficient photoanodic decomposition.[7,8] The situation with CdS is representative; it undergoes photoanodic decomposition according to eq 3. Photocurrent lasts only as long as it takes to form

$$CdS \xrightarrow{2h\nu} Cd_{aq}^{2+} + S + 2e^- \quad (3)$$

an insulating layer of elemental sulfur on the CdS surface. It appears that the photogenerated holes in CdS do have the necessary oxidizing power to effect O_2 evolution from H_2O, but the oxidation of the lattice is kinetically faster. Such seems to be the case with a number of other non-oxide materials, and our efforts since mid-1976 have focused on the problem of learning how to manipulate the relative rates of the various hole processes that may occur.

In 1976 several research groups[21–23] independently reported that CdS and CdSe could be protected from photoanodic decomposition by adding Na_2S and S to the aqueous solution. The dramatic improvement in the constancy of photocurrent from a CdSe-based cell is evident in Figure 1. In this system the oxidation reaction occurring at the photoanode is the oxidation

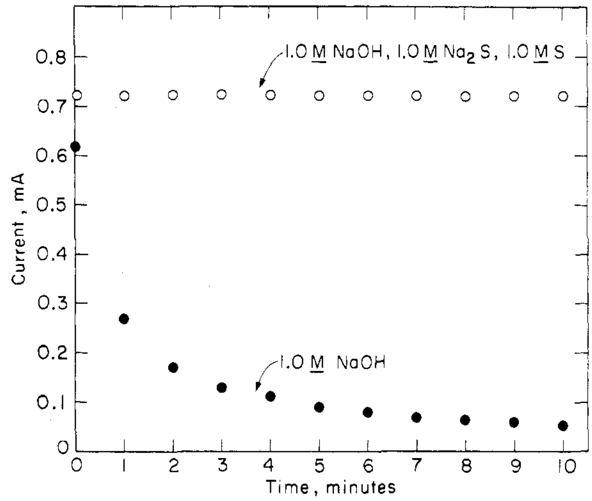


Figure 1. Photocurrent against time for 632.8 nm (~3 mW) illumination of single-crystal (0001 face exposed) n-type CdSe (E_{BG} = 1.7 eV) photoanode in 1.0 M NaOH (●) and 1.0 M NaOH, 1.0 M Na_2S, 1.0 M S (○) aqueous electrolytes with a Pt counterelectrode. The current in the S_n^{2-} electrolyte was continued an additional 48 h without variation. In the absence of S_n^{2-} photocurrent falls rapidly owing to photodegradation of surface. Reprinted with permission from Ellis, A. B.; Kaiser, S. W.; Wrighton, M. S. *J. Am. Chem. Soc.* **1976**, *98*, 6855.

Table II
Non-Oxide Photoanodes Which Can Be "Stabilized" by Chalcogenide Ions

semiconductor	E_{BG}, eV	ref
CdS	2.4	21–25
CdSe	1.7	21–25
CdTe	1.4	21–25
GaP	2.2	24c
GaAs	1.4	24c, 25c,d
InP	1.3	24d
$CuInS_2$	1.4	25e
Bi_2S_3	~1.4	23

of some polysulfide, S_n^{2-}, and apparently not the oxidation of the lattice selenide. At the counterelectrode the reduction of some S_n^{2-} species obtains to give a cell where no net chemical change results. The redox processes occurring at the two electrodes are the reverse of one another, as in Bard's[12] TiO_2-based cell, but the E_{BG} for CdSe is 1.7 eV, giving significant visible response. Such cells thus can be used to sustain the conversion of light to electricity by putting a load in series in the external circuit. The situation is essentially that shown in Scheme II, and the objective would be to optimize the product of photocurrent and voltage for a given input optical power.

The sustained use of other non-oxide photoanodes depends on being able to protect them from photoanodic decomposition. Accomplishing this by adding reductants to the solution sacrifices the ability to directly oxidize H_2O (or any other reductant), but oxidation of the additive may be valuable in its own right, or if the oxidation can be reversed at the counterelectrode conversion of light to electricity can be effected.

It has now been established[24,25] that a number of

(18) (a) Wrighton, M. S.; Morse, D. L.; Ellis, A. B.; Ginley, D. S.; Abrahamson, H. B. *J. Am. Chem. Soc.* **1976**, *98*, 44. (b) Ellis, A. B.; Kaiser, S. W.; Wrighton, M. S. *J. Phys. Chem.* **1976**, *80*, 1325.

(19) (a) Nozik, A. J. *Annu. Rev. Phys. Chem.* **1978**, *29*, 189. (b) Bard, A. J.; Hardee, K. L. *J. Electrochem. Soc.* **1977**, *124*, 215. (c) Kung, H. H., Jarrett, H. S.; Sleight, A. W.; Ferretti, A. *J. Appl. Phys.* **1977**, *48*, 2463.

(20) Bolts, J. M.; Wrighton, M. S. *J. Phys. Chem.* **1976**, *80*, 2641.

(21) Ellis, A. B.; Kaiser, S. W.; Wrighton, M. S. *J. Am. Chem. Soc.* **1976**, *98*, 1635.

(22) Hodes, G.; Manassen, J.; Cahen, D. *Nature (London)* **1976**, *261*, 403.

(23) Miller, B.; Heller, A. *Nature (London)* **1976**, *262*, 680.

(24) (a) Wrighton, M. S.; Ellis, A. B.; Kaiser, S. W. *Adv. Chem. Ser.* **1977**, *No. 63*, 71. (b) Ellis, A. B.; Kaiser, S. W.; Wrighton, M. S. *J. Am. Chem. Soc.* **1976**, *98*, 6418, 6855; **1977**, *99*, 2839. (c) Ellis, A. B.; Bolts, J. M.; Kaiser, S. W.; Wrighton, M. S. *Ibid.* **1977**, *99*, 2848. (d) Ellis, A. B.; Bolts, J. M.; Wrighton, M. S. *J. Electrochem. Soc.* **1977**, *124*, 1603.

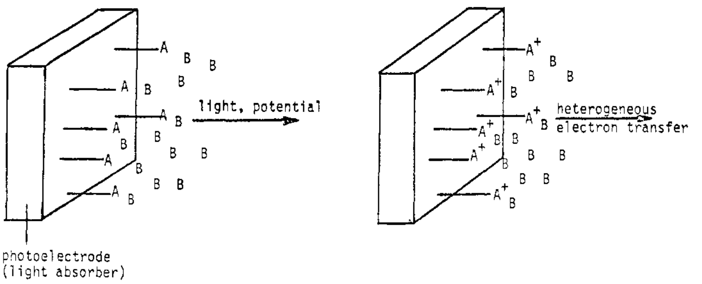


Figure 2. Pictorial representation of mediated oxidation of solution species B where A is the electrode-attached electroactive species. Reprinted with permission from Bolts, J. M.; Bocarsly, A. B.; Palazzotto, M. C.; Walton, E. G.; Lewis, N. S.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 1378.

non-oxide, n-type photoanodes can be protected from decomposition by at least one of the X_n^{2-} (X = S, Se, Te) systems. A list of photoanodes and their band gaps which can be used are given in Table II. A number of these electrode materials in the X_n^{2-} containing electrolyte solutions yield fairly efficient (>5% efficiency) solar cells.

Nonaqueous solvents can be used to dissolve a large number of organic and organometallic redox couples which have fast heterogeneous electron-transfer rates and which have formal potentials covering much of the electrochemical potential scale. Bard's studies of semiconductor/nonaqueous electrolyte systems has provided for the location of the semiconductor band edges on the electrochemical scale. Further, the studies revealed the presence of electrochemically important surface electronic levels situated between E_{VB} and E_{CB}. Such surface and interface states may play a crucial role in the overall kinetics in many liquid junction devices.[26,27]

Bard and Wrighton[7] pointed out that nonaqueous solvents could offer some advantage with respect to thermodynamics for photoanodic decomposition. Shortly after this assertion it was determined that I^- could serve as the reductant in an n-type CdS-based cell for sustained electricity generation when CH_3CN is the solvent.[28] *In H_2O, the I_2 or I_3^- oxidation product from I^- will oxidatively react with CdS in the dark*, but in CH_3CN it is apparent that $E_D°$ is more positive than the I^-/I_3^- couple. The $E_D°$ is certainly more positive for CdS in CH_3CN than in H_2O, since Cd^{2+} is likely solvated better in H_2O than in CH_3CN. That the I_3^-/I^- couple is more negative in CH_3CN is likely useful as well.

In the fall of 1977 we reported our results on the sustained conversion of light to electricity using an n-type Si-based photoelectrochemical cell employing a nonaqueous, EtOH, electrolyte solution of ferricenium/ferrocene.[29] The significant finding was that ferrocene could completely suppress the growth of insulating SiO_x on the surface of the Si photoelectrode. Formation of SiO_x occurs efficiently, and even trace quantities of H_2O in nonaqueous media are sufficient to provide a source of oxygen for the formation of the SiO_x. Presumably, ferrocene can capture photogenerated holes at a rate which precludes such oxide growth. Subsequently, it was found that ferrocene solutions could be used to obtain constant output from n-type Ge in EtOH solution[30] and from n-type GaAs in CH_3CN solution.[27d] Ferrocene is attractive, since it is a fast, one-electron reductant yielding a product, ferricenium, which is reducible at the counterelectrode. The ferricenium/ferrocene potential is such that a good output voltage can be obtained for n-type GaAs or Si (>0.5 V at open-circuit).[27d,29] n-Type Ge yields a low output voltage and has a small band gap (~0.7 eV).[30]

Thus far, the best solar efficiency (~12%) for electricity generation remains with the n-GaAs/Se_2^{2-}/Se^{2-} aqueous solvent system.[25d] However, nonaqueous electrolyte cells of 1–5% will likely be common without significant efforts toward optimization. Further, the nonaqueous media allow for fundamental studies not always possible in H_2O owing to solubility or durability of the semiconductor. For example, we have recently examined the interface energetics for n-type MoS_2 (E_{BG} = 1.75 eV) in CH_3CN or C_2H_5OH electrolyte solutions.[31] The data allowed a very accurate assignment of the value of E_{FB} at +0.30 V ± 0.05 vs. SCE. The position of E_{VB} is even more positive than that for CdS and about the same as TiO_2.[27] This result suggests that visible light generated holes in MoS_2 are indeed very powerful oxidants.

Chemically Derivatized Semiconductor Photoelectrodes

The discovery[29] that ferrocene could completely suppress the formation of SiO_x formation on n-type Si prompted us to consider immobilizing ferrocene centers onto the surface of semiconductors in order to protect them from destructive photoreaction while also allowing the photosensitive material to be useful in oxidizing or reducing substances other than ferrocene. In particular, we had in mind designing photosensitive interfaces which would be rugged and could be used to effect thermodynamically uphill oxidation reactions ordinarily too slow to compete with SiO_x formation at "naked"

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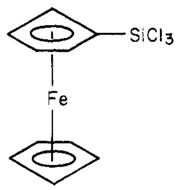
Table III
Electrode Materials Derivatized by Hydrolytically Unstable Ferrocene Reagents, I, II, or III

electrode	comments	ref
Pt Au	reversible, high coverages, very durable, $E°$ within 100 mV of solution ferrocene; Auger and XPES of surface show ferrocene polymer signals	41-44
n-type Si	durable, n-type behavior (photooxidation, dark reduction); photoanodic peak as negative as ~−0.1 V vs. SCE	39, 40, 45, 46
n-type Ge	lower output photovoltage than n-type Si; dark anodic currents observed due to surface states and/or low band gap (0.7 eV)	30
p-type Ge and Si	not fully characterized	47
n-type MoS_2	not fully characterized	48
n-type GaAs	similar to n-type Si, but more output voltage routinely possible	49
n-type TiO_2	not fully characterized, but shows evidence for "surface states" located between E_{CB} and E_{VB}	48

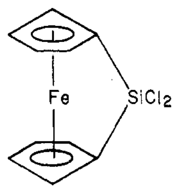
(nonderivatized) Si. The hope was that immobilized ferrocene would be capable of completely efficiently capturing photogenerated holes and would be thereby converted to ferricenium in an uphill fashion. The photogenerated ferricenium would then be capable of effecting oxidation of solution reductants. In principle, any substance which can be oxidized by ferricenium would be oxidizable with the derivatized Si. The essence of the concept is illustrated in Figure 2.

The exciting idea of semiconductor photoelectrode derivatization was further stimulated by the work of Anson,[32] Hubbard,[33] Kuwana,[34] Miller,[35] Murray,[36] and Osa,[37] which was becoming known to us. Their efforts concerning the confinement of electroactive materials to reversible electrode surfaces provided the point of immediate departure for a flurry of activity in my research group during the summer of 1977.

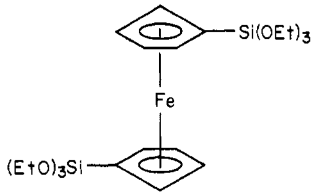
Our approach was to adopt the procedure of surface derivatization using hydrolytically unstable silanes. For this purpose we synthesized the species I–III which have



I



II



III

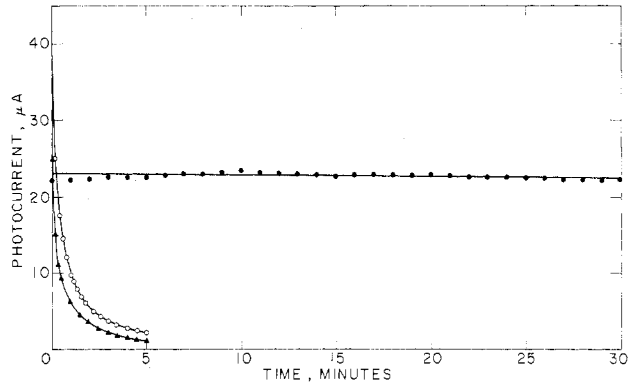


Figure 3. "Stabilization" of n-type Si in aqueous solution by derivatization. Plots of photocurrent against time for a n-Si electrode illuminated with 632.8-nm light. Photoelectrode held at +0.2 V vs. SCE in stirred solutions. Supporting electrolyte is 0.1 M $NaClO_4$ in doubly distilled deionized H_2O. Run 1 (▲), HF-etched "naked" electrode in supporting electrolyte only. Run 2 (○), "naked" electrode re-etched with HF, in supporting electrolyte plus 4 × 10^{-3} M $Fe(CN)_6^{4-}$. Run 3 (●), electrode derivatized with (1,1′-ferrocenediyl)dichlorosilane (II), in the same solution as run 2. Reprinted with permission from Bolts, J. M.; Bocarsly, A. B.; Palazzotto, M. C.; Walton, E. G.; Lewis, N. S.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 1378.

all been used to derivatize electrode surfaces.

Various electrode surfaces have been derivatized with reagents I–III[38–49] and characterized by electrochemical,[38–40,43–45] Auger,[42] XPES,[41] and photoacoustic spectroscopy[50] (Table III). The essential results are as follows. Electroactive material can be persistently attached, and derivatized n-type semiconductors

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generally give light-induced uphill oxidation of the surface-bound material compared to the behavior of reversible materials derivatized with the same reagents. The formal potential, $E°$, for ferrocene confined to the surface of a reversible electrode is about the same as for ferrocene in solution. But on n-type Si, the ferrocene can be oxidized in an uphill sense by ~0.5 V. Further, for derivatized n-type Si the sequence of events occurs as sketched in Figure 2 where B = ferrocene or *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine in nonaqueous media or $[Fe(CN)_6]^{4-}$ in aqueous electrolyte solution. Finally, Figure 3 illustrates the remarkable ability of the derivatized electrode to survive as a photoanode compared to the naked electrode; apparently derivatization does not compromise efficiency for electricity generation, but substantial improvement in durability obtains by inhibiting photogenerated hole processes associated with SiO_x formation.

Derivatized semiconductor photoelectrodes offer a way to design photosensitive interfaces for effecting virtually any redox process. Efforts here are really just beginning and will comprise an important part of our continuing research.

Prognosis

Photoelectrochemistry has already provided the most efficient means of transducing solar energy into chemical fuel (H_2 + $0.5O_2$ from H_2O, ~1%) or electricity (~12%) using man-contrived, wet-chemical systems. There is great interest in this area; many new and good researchers are being attracted into the field. Large numbers of research articles are appearing reporting new systems and higher efficiencies. Significant advances are likely to be made in preparation of large area, thin film photoelectrodes and in surface modification for purposes of manipulating charge-transfer kinetics. The race is on to gain sufficient understanding to provide a scientific base for a new, large-scale energy resource option for use in the first half of the twenty-first century.

The research described above has been possible through the efforts of a very talented and energetic set of colleagues associated with M.S.W. during the last several years. Their research is summarized in the individual references to this article. The different aspects of the research have been supported by various Federal agencies, including the National Aeronautics and Space Administration (oxides, direct H_2 and O_2 generation, laser energy conversion), the United States Department of Energy, Office of Basic Energy Sciences (exploratory interfacial photoredox processes for energy storage, derivatized electrodes for improved durability), and the Office of Naval Research (molecular manipulation of surface state energies). M.S.W. acknowledges support as an A. P. Sloan Fellow (1974–1976) and a Dreyfus Teacher–Scholar Grant Recipient (1975–1980) which provided financial flexibility during portions of this work. Support from the M.I.T. Cabot Solar Energy Fund is also gratefully acknowledged.

Excited-State Chemistry of Cyclopropene Derivatives

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Cyclopropene, a molecule first prepared in 1922,[1] is of current interest from both an experimental and a theoretical point of view. The strain energy in cyclopropene is approximately 54.5 kcal/mol[2] and is primarily due to the strain present in the σ framework. Addition across the double bond in cyclopropene proceeds quite readily since it reduces ring strain by 26 kcal/mol. The relief of ring strain combined with resonance stabilization of the corresponding ring-opened species accounts for the relatively facile ring-opening reaction of this molecule. The work to be reported here originated in the hope that the nature and chemical reactivity of the ring-opened species derived from the irradiation of cyclopropene might be elucidated and that such studies might sharpen our ability to predict or understand the behavior of this transient intermediate when it is generated from other sources. In this Account we review some of the photochemical reactions of cyclopropene derivatives and attempt, using available evidence, to formulate generalizations concerning structure and reactivity relations for these compounds.

Two intermediates have been given serious consideration to explain the products of ring opening of cyclopropene, a diradical **3** and a vinylcarbene **4**.[3] Stretching of the C–C bond in cyclopropene **1**, without rotation of the methylene group, leads to the bisected geometry of the vinylmethylene diradical **2**. Detailed theoretical calculations show that it is the 1,3-diradical singlet state **2** which correlates directly with the ground state and is presumably involved in the thermal cleavage of cyclopropenes.[4] Allowing the CH_2 group to twist leads to structure **3** with a drop of 4.5 kcal in energy for the singlet state. In reality, the thermal

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