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SENSITIZED PHOTOELECTROLYSIS OF WATER WITH SUNLIGHT

Progress Report, June 1—August 31, 1977

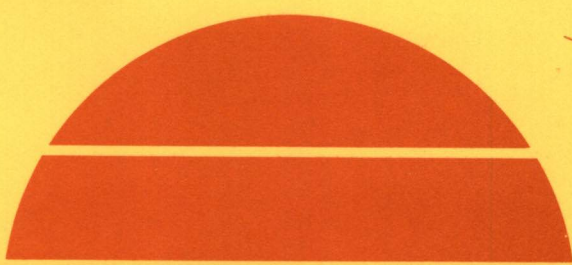
By
Amal K. Ghosh
H. Paul Maruska

September 1977

MASTER

Work Performed Under Contract No. EG-77-C-02-4271

Government Research Laboratories
Exxon Research and Engineering Company
Linden, New Jersey



U.S. Department of Energy



Solar Energy

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SENSITIZED PHOTOELECTROLYSIS
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for Period June 1, 1977-August 31, 1977

Amal K. Ghosh and H. Paul Maruska

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Prepared For

THE U.S. ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
UNDER CONTRACT NO. EG-77-C-02-4271

Exxon Research and Engineering Company
Government Research Laboratories
Linden, New Jersey 07036

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INTRODUCTION

In this project we are investigating the use of heterogeneous catalysts for the sensitized photodecomposition of water into hydrogen and oxygen. The overall objective of this work is to develop superior electrodes for the photoelectrolysis of water by sunlight to produce a valuable fuel, hydrogen. Specific research objectives are:

- (1) To identify combinations of host materials and transition metal dopants which give superior performance as photoelectrolysis electrodes,
- (2) To investigate various combinations of cladded structures (heterostructures) which show promise as photosensitive electrodes, in terms of stability and degree of conversion of water to hydrogen.

The present work was originally started in 1975 at Exxon under a grant from NSF (Grant No. ERP75-13901), and was funded by the company from July 1, 1976 to May 31, 1977. The work done in our laboratory during this period will be reviewed in this first Quarterly Report as part of the review article, in which the work being done in the various other laboratories engaged in research on water photolysis will also be discussed.

Our statement of work for this project comprises the following tasks:

Task A. Literature Review.

Task B. Preparation, Testing and Evaluation of Doped Electrodes.

Task C. Preparation, Testing and Evaluation of Heterostructures.

Task D. Preparation of Reports.

Task A has now been completed, and work on Tasks B and C has commenced.

A. Literature Review

A paper reviewing all of the work which has been done on water photoelectrolysis, from 1839 up to the present, has been prepared. The literature on photoelectrolysis was thoroughly searched (by computer) and 119 references are included with the manuscript. Critical interpretations of the important concepts of this area of investigation have been given in the paper. The theory of semiconductor-liquid junctions which is currently available has been described. Techniques for improving the response of cells are discussed, and the expected maximum sunlight conversion efficiency (of sunlight to hydrogen) for this system has been calculated.

B. Preparation, Testing and Evaluation of Doped Electrodes

Six single crystal boules of TiO_2 were ordered and received from NL Industries. The dopants requested were, respectively, Cr, Mn, Fe, Co, Ni, and Cr + Al. The dopant concentrations were specified as 0.5 wt.% (as the

oxide). Wafers 1 mm thick were sliced from each of the crystals, and the slices were heated in hydrogen in an induction heated furnace to render them conducting. Indium contacts were placed on the back of each wafer, and then the entire wafer except for the front face was coated with epoxy. These electrodes have all been tested in photoelectrolysis cells, and the results are being evaluated. This phase of the work will be presented at the Fall Meeting of the American Ceramic Society in Montreal, Quebec, on September 20, 1977, and will be described in detail in the next Quarterly Report.

C. Preparation, Testing and Evaluation of Heterostructures

For this phase of the work, we are attempting to provide pin hole free layers of SrTiO_3 for use as the outer stabilizing material in the heterostructure. For this purpose we have cut and polished ten slices of single crystal SrTiO_3 to a thickness of 3 mils (75 microns) each. The next step will require the deposition of smaller band gap materials such as CdS and CdSe onto these thin wafers. As a preliminary step, we have succeeded in depositing CdS layers onto glass slides from a solution of CdCl and thiourea. We shall also now investigate vacuum deposition of these materials.

PLANS FOR NEXT QUARTER

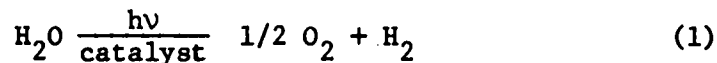
Testing and evaluation of the doped titanate photoelectrodes will continue. Evaluation will include determination of quantum efficiencies of carrier generation and hydrogen formation, spectral response, effect of cell parameters and junction quality. Tests will be performed in actual sunlight for all electrodes which show a promising response. Preparation and testing of heterostructure devices will proceed in the same manner.

Photocatalytic Decomposition of Water
at Semiconductor Electrodes

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1. Introduction

The current energy crises has created a tremendous interest in discovering new sources of fuel to increase our dwindling resources. In the following article, we shall review one aspect of this search, concentrating on the specific chemical reaction which involves the sensitized photodecomposition of water to form oxygen and hydrogen, an extremely important fuel:



The system employs an abundant raw material (water) and produces a fuel (hydrogen) which may be readily stored and shipped. This fuel can be used not only to provide heat for environmental control and cooking, but also to conveniently produce electrical power efficiently, cleanly, and cheaply, in a fuel cell or engine generator. In addition, the hydrogen can be used as the basic raw material for producing other clean fuels and valuable chemicals from various sources such as coal and shale.

In 1974, Paleocrassas (1) wrote a review article on "Photocatalytic Hydrogen Production." Since that time there has been a tremendous explosion of information and work on this subject. The present article will attempt to avoid overlapping with the earlier report. The discussion will

be limited to the photosensitized oxidation of water at semiconductor electrodes. Therefore it will not include photoelectrochemical solar cells or photogalvanic devices (where no net chemical products are created but power is drawn from the cell in the external circuit).

2. The Decomposition of Water

The outstanding natural example of the sensitized photodecomposition of water is photosynthesis. The sensitizer in this case, chlorophyll, absorbs sunlight and catalyzes the decomposition of water. The oxygen from the decomposition is released to the atmosphere while the hydrogen is used to reduce carbon dioxide to carbohydrates. The efficiency of photosynthesis, however, is quite low (highest about 1%) and produce a fuel (carbohydrates) most suitable for use only as food.

The direct formation of hydrogen by photolysis of water has been investigated by many workers. The energy required to photoexcite water directly to the triplet state (which in turn will decompose to hydrogen and oxygen) has been found to be in the region of 190-310 nm (6.5-4.0 eV).⁽²⁻⁷⁾ Unfortunately, this is well outside most of the solar energy spectrum available on earth (350-1100 nm or 3.5-1.1 eV). However, water may be decomposed to hydrogen and oxygen electrochemically (heterogeneously) with a potential difference of only about 1.23 volts. This potential difference is equivalent to a 1000 nm photon.⁽¹⁾ Therefore, if light of this wavelength could be used effectively in an electrochemical cell, it should be theoretically possible to decompose a molecule of water using just two of these photons. Actually, in any practical electrolysis cell, there are over-potentials and other losses, which will be discussed in more detail later.

The high energy required for direct photolysis is the result of the formation of radical intermediates such as H and OH. It is necessary to pass over a high potential barrier, but the energy difference between the initial (H₂O) and final (H₂, O₂) states is only 1.23 eV. This is obviously an excellent situation for catalysis. Conventional electrolysis is a catalytic process involving adsorption of the ionic species OH⁻ and H⁺ on metallic electrodes, but the high cost of electricity makes this process unsuitable for the large-scale generation of hydrogen. However, if sunlight could be used to provide the energy for the electrolysis, then an economically feasible system could result. One way that such a system could be arranged in a straightforward manner would be by connecting currently available photovoltaic solar arrays to existing electrolysis units, but the cost of electricity from silicon solar cells is even more prohibitive than from other sources. What is needed to accomplish photoelectrolysis in a simple, inexpensive manner is an electrode material which can directly absorb the incident sunlight and utilize this energy to drive the water splitting reaction. One excellent possibility appears to be a photosensitive semiconductor electrode.

3. Semiconductor Electrodes

Photoelectrochemical effects at semiconductor surfaces have been known for a long time. Indeed, the first description of a photocurrent due to illumination of a semiconductor electrode (AgCl) with sunlight was given by Becquerel in 1839 ⁽⁸⁾, although little further work was done on this topic for the next hundred years. Then in 1955, Brattain and Garrett ⁽⁹⁾ made a classical investigation of the effects of light on Germanium in

contact with an electrolyte, while in 1960 Richard Williams ⁽¹⁰⁾ studied this process with a number of compound semiconductors, viz., CdS, CdSe, CuI, ZnO, ZnS, ZnTe, and GaAs. A number of other investigations with various materials followed ⁽¹¹⁻¹⁷⁾. Many of the fundamental theories of semiconductor electrodes in contact with solutions were formulated by Gerischer in several publications ⁽¹⁸⁻²⁰⁾ between 1960 and 1970.

Basically, a semiconductor may exhibit conductivity which is either n-type (mobile electrons in the conduction band) or p-type (mobile holes in the valence band). These mobile charge carriers in the semiconductor electrode (electrons or holes) were shown to interact with various redox couples in the solutions. A semiconductor does not have a continuum of electronic energy states (it has a band gap), and therefore a semiconductor electrode differs from a metal because in a semiconductor there are only certain particular energy levels - the valence band, the conduction band, (plus any surface states) - which can interact with ionic species in the electrolyte. Oxidation of ions in the solution can occur under conditions of anodic (positive) bias via the conduction band in n-type materials and via the valence band in p-type materials. Reduction proceeds with cathodic (negative) bias again via the conduction band in n-type materials and via the valence band in p-type materials.

Oxidation currents for anodically biased n-type semiconductor electrodes are not seen unless the potential of the redox couple in the solution is at least as negative* as the potential of the conduction band at the interface, and conversely, reduction currents for cathodically biased p-type semiconductor electrodes only exist if the potential of the

* Negative potentials indicate energy levels closer to vacuum level.

redox couple in the solution is at least as positive as the potential of the valence band at the interface. For redox couples located at energies within the region of the forbidden energy gap for either type of semiconductor, and for redox couples anodic of the conduction band for an n-type electrode or cathodic of the valence band for a p-type electrode, no electrochemical reaction should occur and no currents should flow. Therefore, this system is the analogue of a metal-semiconductor Schottky barrier junction.

There is generally a space charge region at the semiconductor-electrolyte interface, due to differences in the electrochemical potential of the two regions, and consequently the bands in the semiconductor are usually bent upward in n-type materials (electron depletion region formed) and downward in p-type materials (hole depletion region formed). The band bending is increased by anodic bias for n-type materials or cathodic bias for p-type materials, and eventually a potential for the electrode can be reached at which carriers will tunnel. For example, with an n-type material, tunnelling can occur from a redox level located anodic of the conduction band at the interface (located at an energy level between the valence and conduction bands), through the triangular potential barrier in the semiconductor depletion region, to states lying at lower energies (more anodic potentials) in the conduction band in the interior of the semiconductor. This situation is shown schematically in Figure 1. This case is analogous to reverse bias breakdown (by the Zener mechanism) in a solid-state device. So the semiconductor-liquid electrolyte junction can act like a diode and show rectifying behavior. The determining factor

is the difference in electron affinity of the semiconductor and the electrochemical potential of the ionic species in the solution, in the same way that the work function of a metal will determine if a metal-semiconductor contact is ohmic or rectifying.

The semiconductor-solution interface is considered to be composed of three capacitances in series: the semiconductor space charge region, the Helmholtz layer (adsorbed ions) in the solution, and the solution diffuse double layer (Guoy layer). At high ionic concentrations in the solution the capacitance of the diffuse double layer can be neglected. The capacitance of the Helmholtz layer, C_H , is expected to be much larger than that of semiconductor space charge layer, C_{SC} , and therefore the Mott-Schottley relationship gives

$$\frac{1}{C_{SC}^2} = \frac{2}{q\epsilon\epsilon_0 n_0} \left(V - V_{fb} - \frac{kT}{q} \right) \quad (2)$$

where: q = electronic charge

ϵ = semiconductor dielectric constant

$\epsilon_0 = 8.85 \times 10^{-14}$ coul/V-cm

n_0 = carrier concentration

V = applied voltage

V_{fb} = potential at which the semiconductor bands are flat

Studies (16, 17) have shown that this relationship is indeed satisfied for most of the systems tested, and from the straight line obtained on C_{SC}^{-2} vs. V plots, n_0 and V_{fb} have been determined for a number of materials.

4. Semiconductor Electrodes Under Illumination

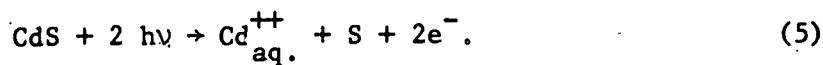
When light is applied to a semiconductor-liquid electrolyte system, it becomes possible to obtain a photovoltage and a photocurrent, in analogy to a solid state photovoltaic device. For example, in the case of an n-type material in contact with a solution, the illumination creates excess electrons in the conduction band and excess holes in the valence band, so that the quasifermi levels for electrons and holes are shifted according to:

$$\Delta E_{Fn} = kT \ln \frac{n_o + n^*}{n_o} \quad (3)$$

$$\Delta E_{Fp} = kT \ln \frac{p_o + p^*}{p_o} \quad (4)$$

where n_o , p_o are the equilibrium carrier concentrations in the dark ($n_o \gg p_o$) and n^* , p^* are the excess carriers from the illumination. Since in an n-type material p_o is very small, ΔE_{Fp} will be very large. On the other hand, n^* may not even be as large as n_o if the light is not very intense, thus changes in ΔE_{Fn} will be small. It is clear that the major effect will involve the minority carriers (holes). It is then possible for oxidation processes which were forbidden in the dark to occur via the optically generated minority carriers in the valence band, and this effect has been observed many times. The rate of the electrochemical reaction is determined by the kinetics of the optically generated minority carriers. A sketch of the type of I-V characteristics which is encountered for semiconductor-liquid junctions is shown in Figure 2, both in the dark and under illumination.

Thus, by 1970 a considerable amount of study had been given to the properties of semiconductors in contact with electrolytic solutions, and theories had been formulated explaining many of the results. However, although this topic had been a fruitful area for research, it had not developed much practical significance (outside of providing some etching techniques). There was a critical problem encountered with all of the materials tested: corrosion (10, 20). In some cases the semiconductors corroded spontaneously in the dark (forming essentially a battery), while in most cases corrosion did not occur unless the electrode was illuminated. Instead of oxidizing reduced species in the aqueous electrolyte, holes in the n-type semiconductor valence band were found to oxidize the electrode itself. Holes in such an n-type semiconductor represent broken bonds, while electrons in a p-type semiconductor are excess bonds, so that in either case accumulation of the photogenerated carriers at the surface can lead to a rupturing of the lattice. For example, with n-type CdS the reaction with light is



The two electrons can reduce Cd^{++} at a counter-electrode. The coating of elemental sulfur covers the surface in a few minutes and the reaction ceases.

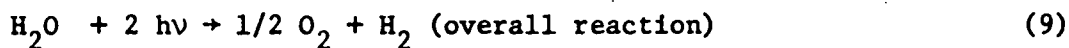
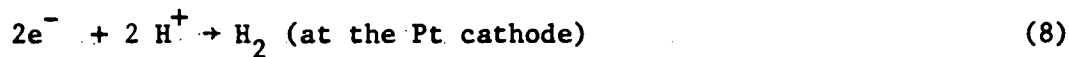
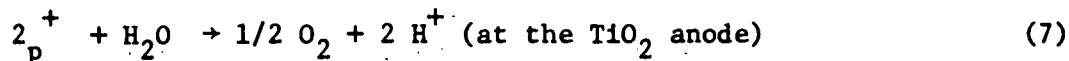
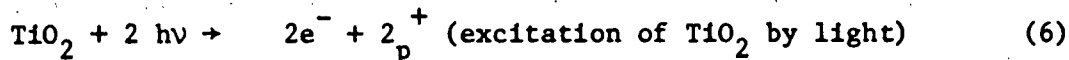
Of course, if an electrode would remain stable under illumination, then it could be used to generate useful chemical products in a solution, while itself only acting as a photocatalyst. As we mentioned earlier, one of the most useful chemical reactions is the electrolysis of water. This

reaction requires the application of at least 1.23 V between two electrodes, although overvoltage problems actually require that 1.6-1.8 V be applied to drive significant currents. The hydrogen produced in this process is a very valuable chemical, even more so today with the shortages of natural gas and oil. If sunlight could be used to drive the water electrolysis reaction this would be an extremely important way to achieve energy independence, since both sunlight and water are abundant, inexhaustible resources.

Now, it is certainly possible to power a conventional water electrolysis unit with electricity derived from single crystal silicon photovoltaic devices exposed to sunlight. This has recently been demonstrated using a solar array panel from the Mariner 4 spacecraft ⁽²¹⁾, but the authors admitted that hydrogen produced by this technique would be very expensive due to the very high cost of silicon solar cells. But in 1972, Fujishima and Honda ⁽²²⁾ showed that it is possible to use the semiconductor TiO_2 (rutile) in contact with water to generate both hydrogen and oxygen under illumination, and claimed that the material suffered no degradation. This report soon created great new interest in the field of semiconductor-electrolyte interfaces.

5. Water Photoelectrolysis at TiO_2 Electrodes

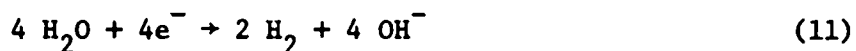
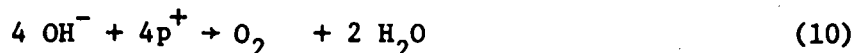
The water photoelectrolysis cell demonstrated by Fujishima and Honda was a major breakthrough because for the first time a semiconductor electrode was found which remained stable in an aqueous solution under illumination. In their cell, oxygen was evolved at the anode (TiO_2) and hydrogen at the cathode (Pt), and the following reactions in their acidic electrolyte were postulated:



They estimated a quantum yield of 10% when the TiO_2 was irradiated with a 500 W Xenon Lamp. After operation, no titanium was detected in the solution. Wrighton and coworkers ⁽²³⁾ confirmed that illuminated TiO_2 is indeed stable in solution. The identity of the gases evolved at the TiO_2 electrode in their experiment was determined by irradiation of the TiO_2 in a 1 M NaOH $\text{D}_2^{18}\text{O}/\text{D}_2^{16}\text{O}$ (1/4) solution. One expects that from such a solution the ratio of $^{16}\text{O}_2$ to $^{16}\text{O}^{18}\text{O}$ should be 2:1, and indeed this was found, suggesting that the reaction is not simply photorelease of oxygen from TiO_2 ⁽²³⁾. This conclusion was further substantiated by these workers through careful weighings of their samples, which indicated no weight changes even after more moles of O_2 were generated than the moles of TiO_2 present as the electrode.

There was a report by Harris and Wilson ⁽²⁴⁾ that aging effects, such as losses in quantum efficiency and changes in surface morphology, were encountered with illuminated TiO_2 anodes operated in 1.0 N H_2SO_4 . However, the Handbook of Chemistry and Physics lists TiO_2 as soluble in H_2SO_4 ⁽²⁵⁾ even in the dark, and experiments we have performed in our laboratory on very thin films of TiO_2 confirm that there is some solubility in sulfuric acid. Most experiments on photoelectrolysis with TiO_2 have

in fact been carried out in strongly basic solution, such as the previously discussed tests of Wrighton, et al. In an alkali solution, again neglecting mechanistic details, the oxygen and hydrogen reactions in a photoelectrolysis cell are:



A representative I-V characteristic found in our laboratory for TiO_2 in 5 M KOH solution, in the dark and illuminated with a 200 W mercury lamp, is shown in Figure 3. Notice that although intense illumination shifts the potential for oxygen generation from anodic values (equilibrium potential for the OH^-/O_2 couple = + 0.16 V vs. SCE) to - 1.03 V vs. SCE, the potential for hydrogen generation at the dark Pt counterelectrode is - 1.07 V vs. SCE, and therefore the cell will not operate spontaneously. Various investigations have established that an anodic bias is always required for water decomposition with illuminated TiO_2 . The minimum bias is 0.15-0.25 V (23, 26) and this can be supplied by a battery, but a number of articles (27-31) have reported supplying the bias chemically, by placing the TiO_2 electrode in the basic solution while using an acidic solution for the Pt counterelectrode (and a salt bridge connecting the solutions). A difference in pH of 13 between the solutions will supply a bias of 0.78 V, and vigorous generation of gases has been seen when such TiO_2 cells are illuminated.

It has been determined that photoelectrolysis of water proceeds spontaneously (no bias required) in cells where the TiO_2 anode is replaced with a related compound, SrTiO_3 (32-34). SrTiO_3 is also quite stable under illumination. Again for this material, Wrighton and coworkers (33) determined the stability by weighing samples and labeling the water with ^{18}O , as described earlier.

6. Bias Requirements for TiO_2 and SrTiO_3 Electrodes

The necessity for a bias voltage (or a differential cell) for TiO_2 but not for SrTiO_3 in a photoelectrolysis cell has been the subject of some study, in our laboratory and elsewhere (32). A clear picture of the relations of the energy bands in these semiconductors to the redox levels in the solution should explain this situation. In solid-state semiconductor measurements the energy bands are positioned relative to vacuum, while the presence of a liquid electrolyte necessitates a different reference, namely, the saturated calomel electrode, SCE. As a guide, one may recall that SCE is at +0.24 V from the normal hydrogen electrode NHE, while NHE is about 4.5 eV below vacuum, so that SCE is 4.74 V below vacuum. By convention in electrochemistry, negative potentials are plotted upward on a diagram.

We set up a number of cells using various TiO_2 and SrTiO_3 samples, and we measured open circuit photovoltage, capacitance vs. voltages and current vs. potential. The absolute magnitude of the open circuit photovoltage was found to be as high as 0.72 V for TiO_2 and 0.94 V for SrTiO_3 . The dark fermi level for these semiconductors in contact with a pH = 14 solution was at -0.31 V vs. SCE for TiO_2 and -0.28 V vs. SCE for SrTiO_3 . When flooded with the entire output of the 200 W Hg lamp, the potential of the TiO_2 electrode became -1.03 V while that of the SrTiO_3 electrode became -1.22 V vs. SCE.

The flat-band potential is the potential at which there is no excess charge in the semiconductor in the region of the semiconductor-solution interface, i.e., the condition where there is no band-bending in

the semiconductor. Obviously, the flat-band potential can be determined by the potential of the fermi level under intense illumination. Thus V_{FB} (flat-band potential) must be at least -1.03 V for TiO_2 .

A large number of capacitance-voltage (C-V) measurements were made to help us to determine the flat-band potential V_{FB} of TiO_2 and of $SrTiO_3$ in a solution. From the $1/C^2$ vs. V plots, we determined $V_{FB} = -1.03$ V at pH = 14 for TiO_2 samples, in accordance with the published value (35, 36). In all cases, V_{FB} changed with pH by the factor 0.059 pH. Carrier concentrations determined from the C-V data were consistently in the 10^{20} cm^{-3} range.

From a carrier concentration of 10^{20} cm^{-3} , one can calculate a barrier width of about 10^{-6} cm. However, assuming the mobility of TiO_2 is of the order of unity (37), then the carrier concentration determined by the C-V data appears too large for our measured sample resistivity of 1 Ω -cm. On the other hand, if we take $\mu = 0.1$ and $\rho = 0.5$ Ω -cm, then indeed it is consistent to have 10^{20} carriers/ cm^3 .

Our current-potential measurements were made for a number of TiO_2 and $SrTiO_3$ samples by using a standard three electrode system. In a 5 M KOH solution with pH = 14, the H_2/H_2O redox couple is located at -1.07 V vs. SCE and the O_2/OH^- couple is at +0.16 V. When TiO_2 cells were scanned in the dark, cathodic reducing currents flowed at potentials negative of the hydrogen couple, but only negligible anodic oxidizing currents were found, as shown in Figure 3. When the samples were illuminated with the Hg lamp, little change ($\sim 10\%$ increase) was noted in the cathodic currents, but major increases in anodic currents were encountered, again illustrated in Figure 3. On the scale used, the dark current and the

reducing current are too small to show in the potential range covered, while an anodic photo-current of up to 50 mA/cm^2 was measured. When such a large current flows, hydrogen generation is so rapid that the Pt counterelectrode literally foams. The situation in the potential range of -0.9 to -1.4 V is shown in greater detail in Figure 4. Anodic currents begin to flow upon illumination with TiO_2 electrodes at precisely -1.03 V . However, with SrTiO_3 , the anodic current commences flowing at -1.23 V .

The foregoing measurements show clearly why TiO_2 cells require a small bias, while SrTiO_3 cells can photoelectrolyze water without any bias. In order for a cell to operate spontaneously without any applied bias, it is necessary that with the application of light, the potential for the evolution of oxygen become more negative than the potential for the evolution of hydrogen. For TiO_2 , this clearly does not happen, while for SrTiO_3 it does (Figure 4). Notice that even though a SrTiO_3 cell can operate spontaneously, the application of a small bias will greatly increase the current and therefore improve the cell efficiency. Thus, the effect of an 0.15 V bias on a TiO_2 cell is to move the potential for oxygen evolution just to the negative side of the potential for hydrogen evolution.

The above results allow us to construct the energy-band diagrams for TiO_2 and SrTiO_3 , in the dark and in the light, shown in Figure 5. All potentials are referred to SCE. These diagrams were constructed for a solution with $\text{pH} = 14$, but changing the pH only serves to move the positions of the energy levels in tandem relative to SCE, without otherwise altering their relative placements. Of course, changing the pH of the solution will alter its resistivity and therefore can affect the magnitude

of the photocurrent. With the application of light to TiO_2 , the electron fermi level E_{Fn} rises according to Equation 3, but not high enough to allow the electrons, which must then pass through the external circuit to the Pt, to transfer to the $\text{H}_2/\text{H}_2\text{O}$ level in the solution. The hole fermi level E_{Fp} drops according to Equation 4 sufficiently far down to allow holes to transfer to the O_2/OH^- level, allowing evolution of oxygen. However, if dissolved oxygen is present in the solution, electrons from the Pt are able to transfer to the O_2/OH^- level, reducing O_2 instead of H^+ and completing a photogalvanic cell (31, 38). With a small negative bias applied to the Pt in a cell with no dissolved oxygen, though, the electrons acquire enough energy to become capable of reducing hydrogen.

As illustrated in Figure 5 for SrTiO_3 , on the other hand, E_{Fn} becomes more negative than $\text{H}_2/\text{H}_2\text{O}$ upon illumination, and the cell operates spontaneously. As Mavroides and Tchernev first pointed out (31), it is necessary to consider the electron affinity as well as band gap of a material when selecting semiconductors for use as photosensitive electrodes. The electron affinity will determine the position of the conduction and valance bands with respect to the $\text{H}_2/\text{H}_2\text{O}$ and O_2/OH^- redox levels, and therefore decide if the cell will require a bias. The electron affinity of SrTiO_3 is less than that of TiO_2 , and therefore SrTiO_3 cells can operate without a bias. The band gap on the other hand, determines what percentage of the available solar spectrum can be utilized by the device. In this respect, neither TiO_2 nor SrTiO_3 are very good photocatalysts for use in sunlight, because with band gaps of, respectively, 3.0 and 3.2 eV, these materials are transparent to more than 90% of the solar irradiation available on earth.

It should now be clear from Figure 5 that the photo-voltage that can be measured in the external circuit only indicates the change in position of the electron fermi level upon illumination, while the total photopotential available for electrolyzing water is the difference between the electron and hole fermi levels. In analogy with a solid state photovoltaic device, one may consider the O_2/OH^- redox couple to be a contact to the valence band while the H_2/H_2O redox couple acts as a contact to the conduction band. Therefore the maximum photovoltage one can obtain from this device is the potential difference between the electron and hole fermi levels. In analogy with a solid state photovoltaic device, one may consider the O_2/OH^- redox couple to be a contact to the valence band while the H_2/H_2O redox couple acts as a contact to the conduction band. Therefore the maximum photovoltage one can obtain from this device is the potential difference between the O_2/OH^- and H_2/H_2O redox levels, namely, 1.23 V, and consequently for direct comparison with solid state photovoltaic devices, one should calculate the power available from a photoelectrolysis cell as the product of this photovoltage, 1.23 V, and the photocurrent.

7. Energy Balance for Photoelectrolysis

Nozik has considered the energy balance in a photoelectrolysis cell in detail (28, 39). For a Schottky barrier device with an inert counterelectrode as shown in Figure 6

$$E_g + V_A = V_B + (E_c - E_f) + \frac{\Delta G}{nF} + \eta_a + \eta_c + iR + V_H \quad (12)$$

Here, E_g is the semiconductor band gap, V_A is any applied external bias, V_B is the band bending at the semiconductor surface, E_c is the conduction band energy, E_f is the fermi level, $\Delta G/nF$ is the free energy change per electron for the chemical reaction, η_a and η_c are the respective overpotentials at the anode and cathode, iR is the Ohmic loss, and V_H is the potential drop across the Helmholtz layer in the electrolyte. The band

bending potential V_B supplies the energy for separating the optically generated hole-electron pairs. Even though the open circuit photovoltage which is measured in the external circuit is determined by the band bending, it should be stressed that the band bending potential does not always contribute to the chemical energy stored in the system. The potential for water electrolysis is not simply supplied by the sum of the band bending plus the external applied bias, as some have claimed (29, 40), and, indeed, the total energy output (stored chemical energy plus electrical energy) is not only as great as the band bending, as others have asserted recently (41). In fact, only if a load resistance is placed in the external circuit, between the active-and counter-electrodes, will the band bending determine the electrical energy available from the cell. Such a situation applies for an electrochemical photocell, like the CdS/Na₂S-S cell, where the same redox couple (i.e., S⁻²/S) undergoes reactions at both electrodes and no net chemical products are formed (42-45).

However, when the function of the cell is water electrolysis, two redox couples (H₂/H₂O and O₂/OH⁻) are involved and the two electrodes are short circuited. The net voltage drop experienced by an electron as it passes through the entire circuit consists of first, an optical excitation from the valence to the conduction band, next, a drop of V_B as it moves to the interior of the crystal, followed by an essentially iso-energetic transfer to the counter-electrode, where it should react with H₂O to form H₂. This electron is stored with the hydrogen; it does not complete the circuit (back to the valence band) until the time that it is allowed to recombine with oxygen formed at the anode. This oxygen, of course, was formed when an OH⁻ ion donated an electron to the valence band. However, if the case

of a semiconductor such as TiO_2 , the electron that is transferred from the conduction band to the Pt electrode lacks sufficient energy to react with the water to produce H_2 . This is analogous to having a series resistance in the circuit, and now the band bending photovoltage must supply energy to the electron to overcome the resistance. With TiO_2 this is still not enough, and a further external bias voltage must also be supplied. But for materials which have their flat band potential far above the hydrogen level (such as GaP), neither the band bending voltage nor an external bias are required.

As further proof of this concept, consider that the open-circuit photovoltages reported for TiO_2 cells are in the range of 0.5-0.7 V (22, 26, 27, 46) and yet with an additional bias of only 0.2 V, water electrolysis results (23, 26). And SrTiO_3 cells with similar open-circuit voltages and no bias requirement are also able to decompose water. The apparent conceptual difficulty is resolved by realizing that only the majority carrier electrons, and not the minority carrier holes, are available for measurement in the external circuit, and so the energy stored in the holes is not considered. Incidentally, if the solution were replaced by a metal to form a normal Schottky barrier, then the hole from the valence band of the semiconductor would simply dissipate its energy as a number of phonons (heat) when it rises up to the fermi level in the metal. In a photoelectrolysis system, this energy can be stored as a chemical product.

Nozik has further proposed that enhanced efficiencies for photoelectrolysis can be achieved if both the anode and the cathode electrodes are optically active semiconductors. Now instead of collecting the majority carrier electrons at the ohmic back contact of the n-type anode material and transferring then through the external circuit to the counterelectrode, the electrons that contribute to the reduction process

are optically generated minority carriers created in a p-type cathode material. The majority electrons from the n-type material and the majority holes from the p-type material constitute a recombination current in the external circuit. In general, the energy balance is

$$E_g(n) + E_g(p) = V_B(n) - V_B(p) + \Delta E_f(p) + \Delta G/nF + \eta_a(n) + \eta_c(p) \\ + iR + V_H(n) + V_H(p).$$

As Nozik pointed out, the maximum energy separation that can occur between the two types of minority carriers, and hence, the maximum energy available for doing chemical work, depends on the electron affinities of the two materials. Consider Figure 7, in which for convenience the term $E_c - E_f$ has been neglected, and no external bias is applied. Now in the case where both the n- and the p-type members are the same material (Figure 7a), the energy separation between the minority carriers can be as large as the band gap (if losses such as over-potentials are negligible). However, in the extreme (if unrealizable) case where two materials have equal band gaps and the flat band potential is the same for the two materials, as in Figure 7b, then the energy available for chemical work will be twice the band gap. This energy is not dependent on the intensity of the illumination of the cell; however, as illustrated in Figure 7c, if a conventional p-n junction device were to be used to drive two external inert (Pt) electrodes to accomplish electrolysis, then the intensity of illumination becomes very important. This feature arises because with the p-n junction device, when the minority carriers cross the junction region and are ultimately collected they actually become majority carriers, and as such are applied to the external platinum electrodes. These collected

carriers suffer energy degradations while traversing the band bending regions on the sides of the junction on which they are in the majority: this loss in energy is exactly the same as the one suffered by the electrons collected from the n-type anode (Figure 6), when they are applied through the external circuit to the inert cathode, as described above. What we have here is an apparent advantage for the photoelectrolysis cell concept: with these cells it is possible to utilize highly energetic minority carriers to drive chemical reactions. And this is accomplished without resorting to the extreme light intensities that would be necessary to obtain an open-circuit voltage equal to the band gap in a conventional p-n junction device, according to

$$V_{oc} = \frac{nkT}{q} \ln bL, \quad (14)$$

where L is the light intensity and b is a constant.

However, caution must be exercised before we conclude that the p-n photoelectrolysis cell leads to higher efficiency. In order for the device to operate, both electrodes must be illuminated. If the two electrodes are the same material, then they will have to be illuminated separately, doubling the area and hence halving the current density. It is important to count the number of photons required for the process. Assuredly, at very low (and therefore impractical) light levels, the voltage from an all solid state device will be negligible, while every photon can generate chemical products in a photoelectrolysis cell. But at sunlight intensities, a silicon solid state device can develop an open circuit voltage of about half the band gap, so that under these conditions a photoelectrolysis cell using silicon and requiring twice the area fails to give an advantage. Note that one might use two semiconductor electrodes with different band gaps placed so as to intercept the light in series

and therefore not require doubling the area. In this case it may be possible to achieve an improvement, but if one of the electrodes has a very wide band gap (such as TiO_2) then the cell current will be limited by the carrier generation rate in that material.

There have been several investigations of cells having both the anode and cathode electrodes as illuminated semiconductors. In all reports, n- TiO_2 was used as the anode and p-GaP was used as the cathode (39, 47-49), although, in addition, n- SrTiO_3 and p-CdTe have also been evaluated (48). When the cathode is illuminated p-GaP, then an illuminated n- TiO_2 anode will allow spontaneous water decomposition (no external bias required) (39). But the reported efficiency of 0.25% in simulated sunlight for this type of device remains low, due to the poor sunlight response of TiO_2 .

Unfortunately, Nozik's energy balance Equation 13 does not allow us to specify the materials we need for an efficient photoelectrolysis cell, because the overpotential terms η_a and η_c are a priori unknown parameters. There are a number of possible causes for overpotentials at electrode; an interesting discussion of this problem has been given recently by Bockris (50). It appears that the major contribution to the overpotential on the TiO_2 anode evolving oxygen under illumination is simply due to the fact that the O_2/OH^- energy level lies quite high above the valence band of the TiO_2 . In this case, if $V_b = 0.7$ and $\Delta E_f \approx 0.1$, then the hole and electron generated by the light will be about 2.2 V apart at the interfaces with the solution. Since C-V measurements (35) have indicated that the $\text{H}_2/\text{H}_2\text{O}$ level is located at approximately V_{fb} for

TiO₂, then the O₂/OH⁻ level is 1.7 V above the valence band. So while this may be considered to be an overpotential, the loss of 1.7 V involved here is independent of the rate of the reaction, and so it does not conform to the Butler-Volmer Equation, as discussed by Bockris (51):

$$J = (\text{const}) [e^{-\alpha nF/RT} - e^{(1 - \alpha)nF/RT}] \quad (15)$$

That is, overpotential is the energy (eV) by which an electron in an electrode material has to be excited above the energy it possessed at thermodynamic reversibility to cause a specific emission rate to an ionic acceptor in the solution (50). It appears that while the loss of 1.7 V may be fundamental to the TiO₂-water system because of the relative placements of the energy levels, in principle, at least, such large "overpotentials" should not be necessary with other materials. However, all oxygen electrodes exhibit overpotentials at significant currents, usually about 0.4-0.5 eV (52). On the other hand, the overpotential for hydrogen evolution on platinum is negligible, and therefore we may use Equation 12 to estimate, the minimum band gap necessary for a Schottky barrier type of photoelectrolysis cell as

$$E_g = 0.3 + 0.1 + 1.23 + 0.5 + 0 + 0.05 + 0.05 = 2.23 \text{ V.} \quad (16)$$

Here we have taken the remaining band bending to be 0.3 V with illumination. Of course, as noted earlier, the energy bands of the semiconductor and the redox levels in the solution must be properly aligned (i.e., correct electron affinity for the semiconductor) in addition to the requirement for a proper band gap energy for the photosensitive electrode.

8. Theory of the Semiconductor-Electrolyte Interface as a Schottky Barrier

a. Wavelength Dependence of the Photocurrent

We have noted a number of times now that the semiconductor-electrolyte interface is considered to behave in a manner analogous to a metal-semiconductor Schottky barrier. This view is taken because the solution is much more conducting than the solid phase, and therefore, essentially all of the depletion region falls within the semiconductor. It should therefore be possible to derive an expression relating the magnitude of the response of a cell to the wavelength of the incident light, and this has been done recently by Ghosh and Maruska (26) for TiO_2 . Briefly, consider a semiconductor electrode of thickness ℓ , with a depletion region of width ℓ_b and a minority carrier (hole) diffusion length L . The number of photogenerated carriers within dx at a distance x from the solution-semiconductor interface is proportional to

$$\phi N_x \exp(-\alpha x) dx \quad (17)$$

where ϕ is the quantum efficiency, N is the number of incident photons, and α is the absorption constant for photons of this wavelength. There are two components to the hole current, one generated in the barrier region and one due to diffusion from the bulk, so that

$$p = \phi N \int_0^{\ell_b} \alpha \exp(-\alpha x) dx + \phi N \int_{\ell_b}^{\ell} \alpha \exp(-\alpha x) \exp[-(x-\ell_b)/L] dx \quad (18)$$

and therefore

$$J = qNG \left[[1 - \exp(-\alpha \ell_b)] + \frac{\alpha}{\alpha + \beta} \exp(\beta \ell_b) \{ (\exp-(\alpha + \beta) \ell_b) - (\exp-(\alpha + \beta) \ell) \} \right] \quad (19)$$

Here J is the photocurrent/cm², $\beta = 1/L$, and G is a factor related to the photoconductive gain in the barrier region as well as to the process governing the transport of the holes across the interface.

Using the absorption spectrum for TiO₂ available in the literature (53) to relate α to λ (the wavelength of incident monochromatic light), Ghosh and Maruska (26) determined that there is a good fit of their experimental data with the relationship given in Equation 19, as shown in Figure 8. They determined that barrier widths were of the order of 10⁻⁶ cm, and hole diffusion lengths were of the order of several microns. Significantly, longer diffusion lengths were found for Al-doped TiO₂ (4.5 microns) than for undoped TiO₂ (1.2 microns). Since in either case the hole diffusion length is much greater than the barrier width, then the photoconductive gain is approximately unity for short wavelength light absorbed entirely within the barrier region. For light with 340 < λ < 420 nm, a larger proportion of carriers are collected in Al-doped TiO₂ due to the improved diffusion from the bulk. In sunlight with a measured intensity of 105 mW/cm², the conversion efficiency (defined as the ratio of the energy stored in the hydrogen produced to the energy of the incident sunlight) was found to be as high as 1.3% for Al-doped TiO₂ cells. A sunlight conversion efficiency of 0.4% had been reported earlier (54) for undoped TiO₂, and a value of 0.6% was published more recently (55). Another report (56) of 0.8% efficiency is questionable because of the low incident solar power (40 mW/cm²) which was assumed (not measured). It may not be possible to use concentrators to increase the cell current, because the photocurrent appears to saturate at high intensities (57).

At shorter wavelengths below about 350 nm, the quantum efficiency has been shown to be constant (23, 26). This constant value is significantly larger for Al-doped TiO₂ samples than for undoped samples (26). It is possible that there are major differences occurring from sample to sample between the bulk values of hole lifetime and mobility and the barrier region values of these quantities. This could explain the differences in the value of G. However, it appears more likely that the rate limiting step is the process of hole transfer to the electrolyte, and this process appears to require the presence of surface states to allow isoenergetic transfer (58). Following the discussion of Boddy (17), one may consider the following sequence of steps for oxygen formation at the surface of TiO₂:



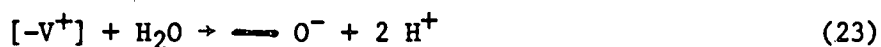
where $\text{--- } \text{O}^-$ is a surface oxygen ion and p^+ is a hole. Then



where $[-\text{V}]$ is an oxygen vacancy. Next



and



This reaction sequence does not indicate an actual corrosion of the semiconductor because only the initial oxygen comes from the structure, with subsequent oxygen coming from the water in a repeated cycle. A discussion of the surface reaction along similar lines has been given by Gissler, et al. (59). Now if Al^{3+} replaces Ti^{4+} at some surface sites in Al -doped TiO_2 , this alteration may increase the probability of Equation 21. Since Al^{3+} introduces one more electron than Ti^{4+} , the structure may relax more readily by creating an oxygen vacancy to compensate for the extra charge. Augustynski, et al. have now also reported improved response for TiO_2 doped with 6% Al_2O_3 (60).

b. Voltage Dependence of the Photocurrent

The derivation given above can be extended to show the dependence of the photocurrent on the voltage across the depletion region. Basically, the connection is made by giving the relationship between the width of the barrier region, l_b , and the voltage, V :

$$l_b = \left(\frac{2\epsilon\epsilon_0}{qNd} \right)^{1/2} V^{1/2} \quad (24)$$

This has been done, for example, by Bulter and Ginley (61) who obtained

$$J = q \Phi_0 \left\{ 1 - \frac{\exp[-\alpha W_0 (V - V_{fb})^{1/2}]}{1 + \alpha L_p} \right\} \quad (25)$$

where $W_0 = (2\epsilon\epsilon_0/qNd)^{1/2}$. Also, Laser and Bard (62-64) used a more exact computer simulator technique to generate these characteristics. In general, agreement with experimental results is excellent at higher voltages (greater than a few tenths of volt), but deviations are found at small voltages. Wilson has proposed (65) that this difficulty is encountered because one of the boundary conditions usually taken is that $p = 0$ at $x = l_b$, which neglects surface recombination. He has instead used the boundary condition,

$$- D \frac{dp}{dx} = S p \text{ at } x = l_b \quad (26)$$

where S is directly related by terms involving the voltage to the sum of the surface recombination velocity and the surface charge transfer reaction velocity. He determined that surface recombination is only important at small values of the voltage, near V_{fb} . Laser and Bard pointed out also that at potentials close to flat band, the photogenerated electrons will not be effectively driven away from the surface, and so a back reaction involving electrons from the conduction band reducing O_2 back to OH^- can occur (64). However, since TiO_2 must be operated at some small anodic bias because of problems with the hydrogen reaction, these difficulties are not encountered in operating cells, and in fact, 100% quantum efficiencies have been achieved.

9. Increasing the Sunlight Response

We have shown now that the theory of semiconductor-solution photoelectrolysis cells has been fairly well developed, except (especially) for the detailed mechanisms of charge transfer across the interface. However, no practical devices have yet been achieved. All electrode materials which have been tested so far suffer from either or both of the following problems:

1. The semiconductor corrodes under illumination.
2. The semiconductor is a poor absorber of sunlight.

A number of approaches are being pursued to overcome these difficulties.

These include (a) new small band gap semiconductors, (b) dye sensitization, (c) heterostructure formation, and (d) impurity sensitization.

a. New Small Band Gap Semiconductors

Many new materials are currently being prepared and tested in various laboratories. For example, there are other titanates such as $SrTiO_3$ (32-34), $BaTiO_3$ (66-68), and $CaTiO_3$. Unfortunately, even though these materials are stable, they have band gaps even wider than that of

TiO₂, SnO₂ (69, 70), KTaO₃ (71) and SiC (72) also possess very large band gaps. WO₃ (73-75) with a band gap of 2.7 eV shows promise, but very little current is generated with photons of energy less than 3 eV, and 100% quantum efficiency is not reached until 275 nm. Apparently this problem is the result of an indirect band gap (74). There are also some stability problems with WO₃ (but it may be stable in certain electrolytes), and in addition it requires a large bias because it has too large an electron affinity. Fe₂O₃ (76-78) also has a smaller band gap, 2.2 eV, and from that standpoint would be ideal. But high efficiencies have not been reported with Fe₂O₃, again due to an indirect band gap (slowly increasing absorption constant) and large electron affinity (77). However, Fe₂O₃ appears to be completely stable, and in fact, it is the only semiconductor with absorption at 550 nm, the peak of the solar spectrum, which exhibits stability. Further work is needed with this material to overcome its defective properties. It is possible to synthesize a number of compounds of the iron oxide-titanium oxide system (iron titanates), but these materials do not show as good a response as either Fe₂O₃ or TiO₂ (79). YFeO₃ has a band gap of 2.6 eV, larger than Fe₂O₃, but it requires less bias (80).

There have recently appeared three publications describing photo-electrochemistry at a large number of oxide semiconductors. Clechet, et al. (81) studied the oxides of titanium, niobium, tantalum, and zirconium, all of which have very large band gaps and therefore poor sunlight absorption. Kohl, Frank and Bard (82) synthesized and tested TiO₂, Fe₂O₃, V₂O₅, WO₃, PbO, Bi₂O₃, CuO, Cr₂O₃, CoO, CdO, MnO₂, and SrO in polycrystalline form. All of these materials except for TiO₂, Fe₂O₃, and WO₃ showed either poor photocurrents or corrosion (or both). Kung, et al. (40) tested TiO₂, SrTiO₃, BaTiO₃, Fe₂O₃, CdO, CdFe₂O₄, WO₃, PbFe₁₂O₁₉, Pb₄Ti₃WO₁₃, HgTa₂O₇, and HgNb₂O₇ and reported that these

were all stable, at least in certain ranges of pH. The band gaps of the cadmium, lead and mercury compounds were determined to be in the range of 1.8 - 2.4 eV, and a photo-response with $Hg_2Ta_2O_7$ was found at wavelengths as long as 650 nm. However, a disturbing trend was discovered: with these particular semiconductors, the smaller the band gap, the larger was the electron affinity, and therefore, the larger was the required bias voltage. There is another survey ⁽⁷²⁾, though, which indicated that there exist a number of smaller band gap materials such as GaAs, GaP, CdSe and CdS which have much smaller electron affinities and hence should not require external bias voltages. The ability of a semiconductor to photoelectrolyze water without an applied bias has been correlated with the electronegatives of the constituent atoms by Butler and Ginley ⁽⁸³⁾.

The more common n-type semiconductors such as CdS, CdSe, GaAs, and Si have been known to be unstable for a long time. As we discussed briefly before, some of these, such as CdS, can be stabilized effectively with proper solutions containing the anion, such as S^{-2}/S , but then no water photolysis results ⁽⁴²⁻⁴⁵⁾. Rather, the sulfur/sulfide couple undergoes the reduction and oxidation, and power can be drawn from the external circuit. This type of cell is outside the scope of this paper. There have been a couple of recent papers describing illuminated Si electrodes ^(84, 85) and CdS electrodes ⁽⁸⁶⁾ where no stabilizing agents were introduced into the water. Two recent review articles have appeared by Gerischer ⁽⁸⁷⁾ and by Williams ⁽⁸⁸⁾ which discuss the corrosion problems suffered by most smaller band gap materials.

A listing of various materials which have been used in photoelectrolysis cells is given in Table I. When values of the flatband potential listed in this chart are positive versus hydrogen, then they indicate the approximate external bias required (negative values indicate spontaneous operation).

b. Dye Sensitization

A large number of dyes are capable of absorbing incident visible light and transferring the excited state to the substrate material. Materials like the silver halides, ZnO and TiO₂ have band gaps of 3 eV and larger and thus intrinsically respond only to uv excitation, but in their normal use for imaging processes, they can be made to respond to sunlight by dye sensitization. For example, a variety of cyanine dyes are known to photosensitize TiO₂ for the photographic process ⁽⁸⁹⁾. With an n-type substrate material such as TiO₂ and the generally p-type dyes, a heterojunction will form. On absorption of photons of visible light by the dye, electron-hole pairs are formed and can be separated at the junction, so that the electrons move into the TiO₂ while the holes are injected into the solution. In general, in a heterojunction, the smaller of the two energy gaps determines the voltage output that can be achieved from the photocell ⁽⁹⁰⁾. Thus, if the dye has a band gap of 2 eV, the voltage differences between the n and p regions should be about 2 V, and this should be sufficient to electrolyze water.

In our laboratory we have studied a number of cyanine, merocyanine, rhodamine, styryl and phenothiazine dyes in our cells. Two techniques were used for depositing the dye on the surface of the TiO₂ wafers: Vacuum deposition and solution dipping. For vacuum deposition the dye was heated in a vacuum system so a thin film 1000Å thick deposited on the TiO₂ by sublimation. For solution dipping, the dye was dissolved in a suitable solvent and the TiO₂ wafer was then dipped into the solution, withdrawn and allowed to dry. No difference in performance could be attributed to the number of coatings of dye used. All cells contained neutral (pH = 7) 0.1 M KCl solution.

Sensitization was determined by measuring a photocurrent in response to visible light, and a number of the dyes were found to respond to the illumination. Peak sensitization wavelengths were found in the range of 450 to 550 nm, in the visible portion of the spectrum. The highest quantum efficiency measured was about 0.7% at 510 nm with several merocyanine dyes, while a cyanine dye showed a peak sensitization at 550 nm with a quantum efficiency of 0.1%. The rhodamine, styryl and phenothiazine dyes which were tested showed very little or no sensitizing effects on TiO_2 in our photoelectrolysis cells, although some of them are known to be strong sensitizers for photographic (non-aqueous) processes (91). These dyes may have been desorbed from the TiO_2 surface during rinsing or while in the electrolyte solution. Tsubomura, et al. (92) reported studying dyes such as Rhodamine B, Rose Bengal, Eosin Yellow, and Acridine Orange adsorbed on TiO_2 and ZnO substrates. They measured quantum efficiencies of 0.1-1.0%. A number of other dyes have also been tested using these substrates (93-98).

The major problem with the dyes studied is the rapid degradation of response. It was found in our studies that the region of the dye-coated electrodes which had been illuminated showed severe bleaching, so that the normal blue color of the TiO_2 rather than the red color of the dye became visible. Current deterioration in all of the dyes was quite rapid, and usually the current dropped by an order of magnitude in a matter of minutes. It is likely that during operation, oxidation of the dye, rather than oxidation of the water, is taking place at the illuminated anode. Even if the process were capable of producing oxygen, it is most likely that this oxygen would then rapidly react with the dye molecules and destroy them. Tsubomura, et al. (92) found that the decay in photocurrent could be restrained by adding the "super-sensitizer" hydroquinone. However, in this situation they did not report the observation of any oxygen evolution, and neither has any other paper. If no oxygen is evolved

from the solution, then some other specie must be undergoing oxidation. In this case it must be the super-sensitizer.

Thus, it has been shown that the organic dyes tested thus far exhibit the same instability problems that are found with most smaller band gap semiconductors. Possibly this system can be used as an electrochemical photocell, where the oxidized super-sensitizer migrates to the counter-electrode to be reduced.

c. Heterostructure Formation

This method of sensitization is an attempt to combine the corrosion resistance of several wide band gap semiconductors with the good sunlight absorbing characteristics of smaller band gap materials. This type of heterostructure device is used with the stable wide band gap semiconductor, which is transparent to most of the incident solar spectrum, in contact with the solution. The optical generation of hole-electron pairs is then expected to occur in the shielded small band gap material, so that subsequent carrier transport through the wide band gap material is essential for the device to operate. There have been attempts to form heterostructure devices by depositing TiO_2 on GaAs, GaP, CdS, CdSe and Si (99-102). A similar approach involved coating GaAs with molybdenum oxide (103). Studies have also been made on structures where a thin metal film, such as gold, was used to protect small band gap semiconductors from corrosion (104-106). Of course, a film of metal sharply reduces the light transmission to the substrate.

Let us first discuss the metal coatings. If the metal film is thick enough to be continuous (free of cracks and pinholes), then the device acts simply as if it were a conventional metal-semiconductor Schottky barrier in series with an electrolysis cell (104). The maximum voltage

available from this device is just the band bending at the metal-semiconductor junction, and this voltage is typically not large enough to decompose water. The energy difference between the optically created hole in the semiconductor valence band and the fermi level in the metal film is dissipated as phonons, instead of contributing to the generation of chemical products. This device would work if it were possible to find some metal which would make contact to the semiconductor at the level of the valence band, so that the energy of the holes would not be dissipated. It has been possible to actually decompose water with an illuminated n-GaP/Au electrode where the gold film was not continuous (105). Here the solution came into contact with the semiconductor through the cracks in the metal film, and it was claimed that corrosion was contained because the gallium hydroxide was held within the cracks instead of peeling away and exposing more GaP surface to corrosion. These heterostructures showed response to visible light up to 550 nm, with a quantum efficiency of 11% at 420 nm and an estimated sunlight conversion efficiency of 1-2%. However, there remains the question of long term stability of these devices, and this problem will require further study.

Overcoatings with wide band gap semiconductors have so far not given very encouraging results. Tomkiewicz and Woodall (102) have studied devices made from n-type GaAs and GaAlAs coated with SnO_2 , Nb_2O_5 , Al_2O_3 , TiO_2 , or Si_3N_4 . As far as they could determine, the films did not suffer from pinholes, yet localized corrosion occurred anyway. They postulated diffusion of some species in the electrolyte through the intact films to the surface of the substrate semiconductor, and they felt that this problem could not be overcome by better sample preparation. Furthermore, they determined that the entire photocurrent was generated in the film and not in the substrate. Perhaps rather than having ions from the

electrolyte diffusing through the film to cause corrosion, photogenerated holes in the film diffuse inward, instead of to the surface, and oxidize the substrate material.

Kohl, Frank, and Bard (101) used chemical vapor deposition to coat n-type TiO_2 onto n-Si, p-Si, n-GaAs, p-GaAs, n-GaP, n-InP, and n-CdS. First of all, crack- and pinhole-free films were not obtained on CdS, GaAs or GaP by this method, and the usual photocorrosion problems were observed. The TiO_2 films deteriorated and eventually fell off. Durable, crack- and hole-free films of TiO_2 were deposited on n-Si and n-InP. The action spectra for n-InP/ TiO_2 and n-Si/ TiO_2 were the same as that found for TiO_2 ; i.e., photoeffects were only found with light of $\lambda < 400$ nm. Similar results were seen for p-type substrates. They concluded that they were not able to inject holes from the small band gap substrate into the TiO_2 , which was hydrogen reduced after deposition and therefore n-type.

It can be seen that the major problem involved here is hole transport. If two n-type materials with different band gaps, but with each having the fermi level close to the conduction band edge, are joined to form a heterojunction, then there will result a barrier in the valence band. And this barrier will prevent the flow of holes from the smaller band gap material to the larger one. It would be possible to extract the holes by tunneling if the outer large band gap film is very thin, but films thin enough to allow tunneling are unlikely to be coherent. The structure which deserves more study is an $n^+ - n$ device in which the fermi levels have been properly adjusted so as to avoid any barrier in the valence band.

d. Impurity Sensitization

An interesting approach for extending the response of a wide band gap material such as TiO_2 to visible light is impurity doping. The excitation of the impurity into the TiO_2 bands can result in free electron and hole formation. This is described by the following equations and Figure 9.

Impurity Sensitization

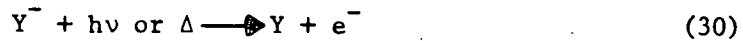


Figure 9(a) shows an electron excited from the impurity level to the conduction band. The ground state level of the ionized impurity level may shift. The hole in the ground state level can ionize by heat or light and result in a free carrier. Figure 9(b) is similar to Case (a) with the exception that the impurity level is roughly midway between bandgap and it does not shift after ionization.

Figure 9(c) shows the case where the catalyst material is doped with two impurities. Optical excitation in these levels gives rise to free electrons and free holes. Obviously the cases described need roughly two photons for excitation. The photons may be of the same energies or one may be much larger than the other.

It has been demonstrated that the transitions described above are possible in solids and in particular in the titanates. (107-112) There are many reports which describe the locations and position of impurity levels (such as Fe, Co, Cr, Mn, V, Ni) relative to the bandgap in rutile and similar materials of interest. (107-111) The transition in some cases is strong and comparable in strength to bandgap excitation. (113, 114)

Ghosh and Maruska (26) have shown that water photoelectrolysis can actually be accomplished using visible light on a Cr-doped TiO_2 electrode. Their cell required a minimum bias of 0.6 V and generated a current of 0.35 mA/cm². All uv light from the Hg lamp source which could have provided band to band transitions was removed with an appropriate filter. Hydrogen and oxygen were collected at the electrodes, and the TiO_2 :Cr remained stable under extended illumination. Further work is in progress to find other dopants which can give stronger absorptions.

Morisaki et al., (115) have also reported photocurrents due to visible light excitation of TiO_2 , and their action spectrum showed a peak response around 800 nm. However, this photocurrent was cathodic, occurring only when the TiO_2 electrode was held at potentials more negative than the $\text{H}_2/\text{H}_2\text{O}$ level. They ascribed this response to excitation of surface states, but it should be noted that reduced TiO_2 shows optical absorption around 1 micron due to defect states (oxygen vacancies or Ti^{3+}). (116) Thus this effect could also have been a case of impurity sensitization.

10. Outlook

Assuming that we wish to use solar energy to obtain hydrogen from water by electrolysis, then the critical question is whether it is possible to find a photosensitive electrode material which will have an efficiency comparable to silicon solid state devices and yet be less expensive. It must be remembered that 4 silicon photovoltaic cells connected in series will be necessary to generate the same voltage for electrolysis as can be achieved by one photoelectrolysis electrode with a 2.2 eV band gap. By counting the number of AM1 sunlight photons which can be absorbed by a material with a 2.2 eV band gap (assumed to be direct so that the absorption constant increases rapidly with wavelength after the absorption edge), we can calculate a maximum photocurrent of 11 mA/cm² (117). The total available solar power at

AM1 is 100 mA/cm^2 , so that the maximum sunlight conversion efficiency for a photoelectrolysis cell may be calculated as

$$\eta = \frac{1.47I}{P_L} = 16\% \quad (31)$$

where 1.47 is obtained from the heat content per mole of hydrogen. If it would be necessary to supply a bias, for example, of 0.4 V, then the maximum efficiency would be 12%. This value compares very well to silicon, especially since only 1/4 of the area is required. Furthermore, even if silicon cells had an efficiency of 20%, a conventional electrolysis unit of 70% efficiency used in conjunction with the silicon devices would give an overall efficiency of 14%. Therefore, we do not concur with the recent conclusion of Manassen et al. (118) that technological prospects of photoelectrochemical decomposition of water is dim; at this time, we do not see a fundamental reason that high efficiencies for this process cannot be attained. But the materials problems remain formidable.

And furthermore, perhaps some attention should be given to driving chemical reactions other than water electrolysis in these solar powered cells. There are numerous organic as well as inorganic reactions that can be run at an illuminated electrode which could produce fuels. Some redox couples have already been tested (58, 119) and current multiplied (due to combined oxidation and reduction at the same electrode) has been observed. (119) It is certainly possible that the corrosion problems exhibited by so many of the small band gap semiconductors will be relieved in a non-aqueous electrolyte.

11. Summary

Although semiconductor electrodes have been studied for a long time, the problem of photocorrosion made them of limited use in practical devices. The discovery that TiO_2 is stable in an illuminated electrochemical cell brought a great new interest to this topic. The photoelectrolysis of water

to provide the useful fuel hydrogen was shown to be possible using a TiO_2 anode. However, the efficiency of hydrogen production in sunlight has been low because TiO_2 is a poor absorber of visible light. A number of techniques for improving the response are now being tried. A number of new semiconductors with smaller band gaps, such as Fe_2O_3 , WO_3 , and p-GaP are being studied. Dye sensitization has only received limited attention, but decomposition problems have again occurred. Formation of heterostructures between stable wide band gap materials and corrosion-prone small band gap semiconductors needs further work, as does the area of increasing the visible light response through impurity doping.

Acknowledgment

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Table I

Semiconductors Tested as Electrodes for Photodecomposition of Water

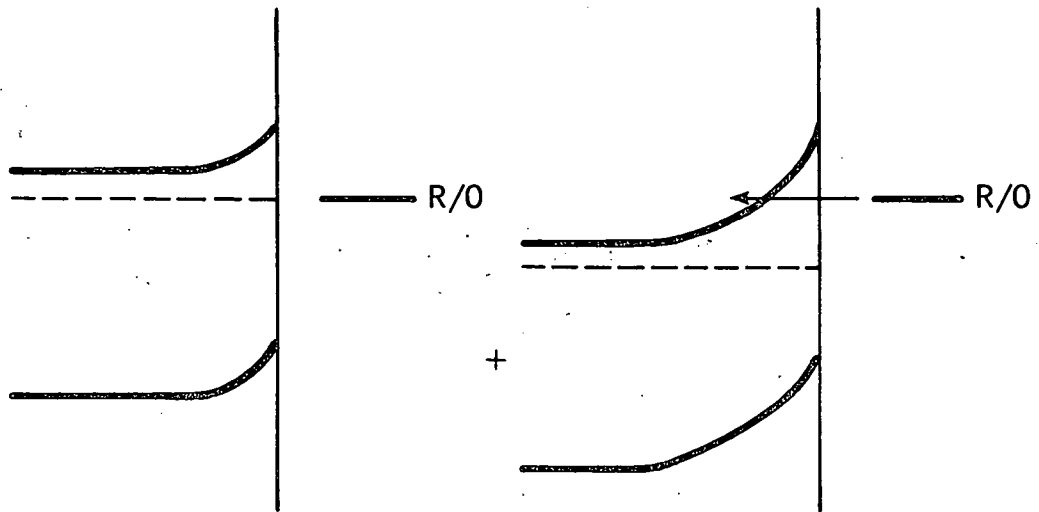
Material	Bandgap E _g	Flatband Potential vs. Hydrogen	Highest Q.E. of Carrier Generation(%)	Remarks	Reference
TiO ₂	3.0	0.05	100	Stable	22-24, 26-31, 36, 40, 82
SrTiO ₃	3.2	-0.2	100	Stable	32-34, 40
BaTiO ₃	3.3	0.1	30	Stable	66-68, 40
KTaO ₃	3.5	-0.2	6	Stable	71
FeTiO ₃	2.2	1.1	15	Leaching of Fe atoms noted	79
Pb(La)TiO ₃	3.0	-	-	Too resistive	66
Pb(La, Zr)TiO ₃	2.9	-	High?	Too resistive	66
Fe ₂ TiO ₄	2.1	1.2	15	Leaching of Fe atoms noted	79
Fe ₂ TiO ₅	2.2	1.5	15	Stable	79
BaTi _{1-x} Fe _x O _{3-xF}	2.8	-	-	Photoresponse quenched	68
Fe ₂ O ₃	2.2	0.7	40	Stable at pH >6	76-77, 82
Cu ₂ O	2.2	-	-	Corrodes	88
CuO	1.7	1.0	-	Corrodes	82
WO ₃	2.7	0.5	100	Stable at low pH	73, 74, 75, 40
ZnO	3.2	0	-	Corrodes	14, 19
SnO ₂	3.5	0.5	100	Stable	69, 70
SiC	3.0	-1.3	-	Corrodes	72
V ₂ O ₅	2.75	1.2	-	Corrodes	82
PbO	2.8	0.45	-	Corrodes	82
Bi ₂ O ₃	2.8	0.7	-	Corrodes	82
YFeO ₃	2.6	0.5	1	Stable	80

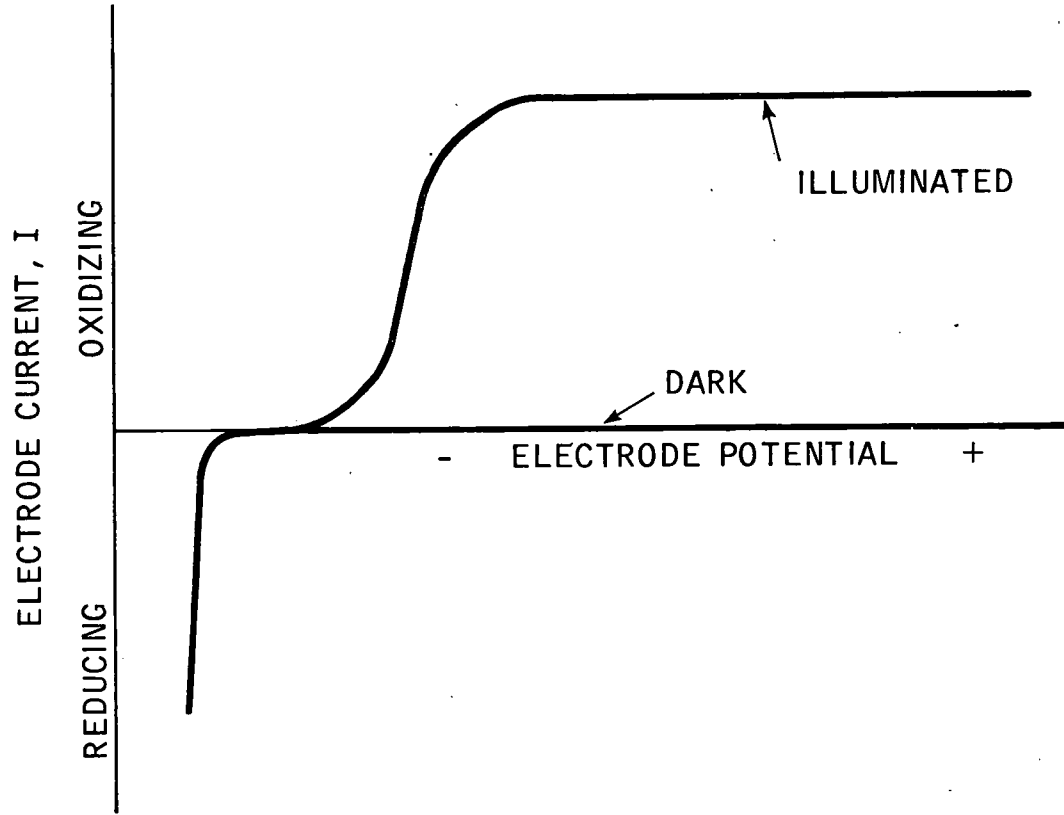
Table I (Continued)

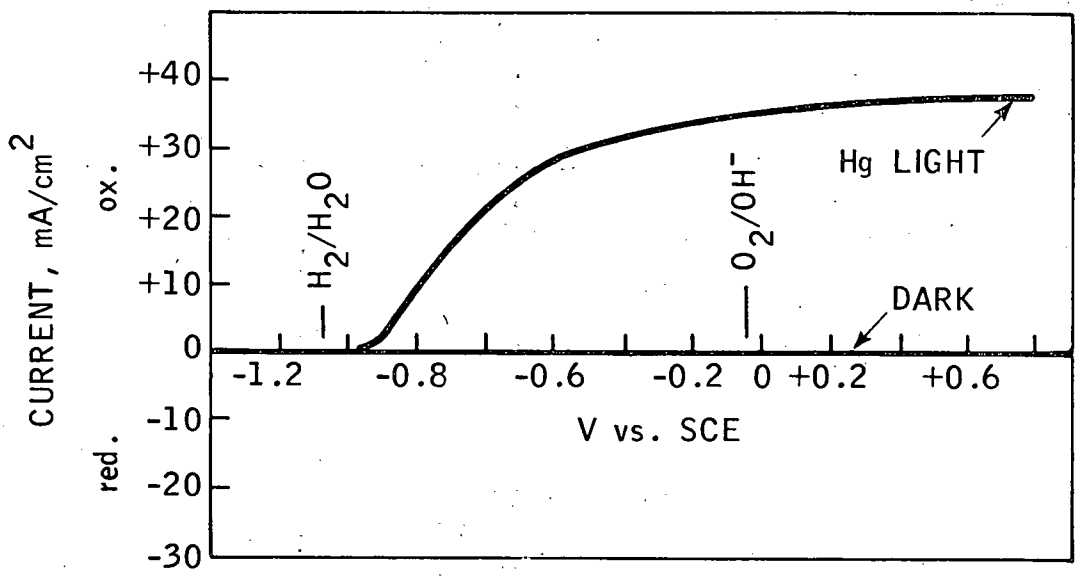
Material	Bandgap E _g	Flatband Potential vs. Hydrogen	Highest Q.E. of Carrier Generation(%)	Remarks	Reference
<u>Cr₂O₃</u>	1.4	-	-	Corrodes, poor response	82
<u>CoO</u>	0.5	0.8	-	Corrodes, poor response	82
<u>CdO</u>	2.3	-	-	No response	82,40
<u>MnO₂</u>	0.3	-	-	No response	82
<u>SrO</u>	5.7	-	-	No response	82
<u>Si</u>	1.1	-0.7	-	Corrodes	84,85
<u>InP</u>	1.3	-0.2	-	Corrodes	101
<u>GaAs</u>	1.4	-0.5	-	Corrodes	101
<u>GaP</u>	2.2	-1.0	-	n-type corrodes, p-type stable	39
<u>CdS</u>	2.4	-0.5	-	Corrodes	86,88
<u>CdSe</u>	1.7	-0.2	-	Corrodes	88
<u>ZnSe</u>	2.6	-	-	Corrodes	88
<u>CdFe₂O₄</u>	2.3	0.8	-	Poor response but stable	40
<u>PbFe₁₂O₁₉</u>	2.3	1.0	-	Stable at high pH	40
<u>Pb₄Ti₃WO₁₃</u>	2.4	0.4	-	Stable at high pH	40
<u>Hg₂Ta₂O₇</u>	1.8	1.2	-	Stable	40
<u>Hg₂Nb₂O₇</u>	1.8	1.1	-	Stable	40
<u>ZrO₂</u>	5.0	-1.0	-	Stable	81
<u>Ta₂O₅</u>	4.0	-0.4	-	Stable	81
<u>Nb₂O₅</u>	3.4	0	-	Stable	81

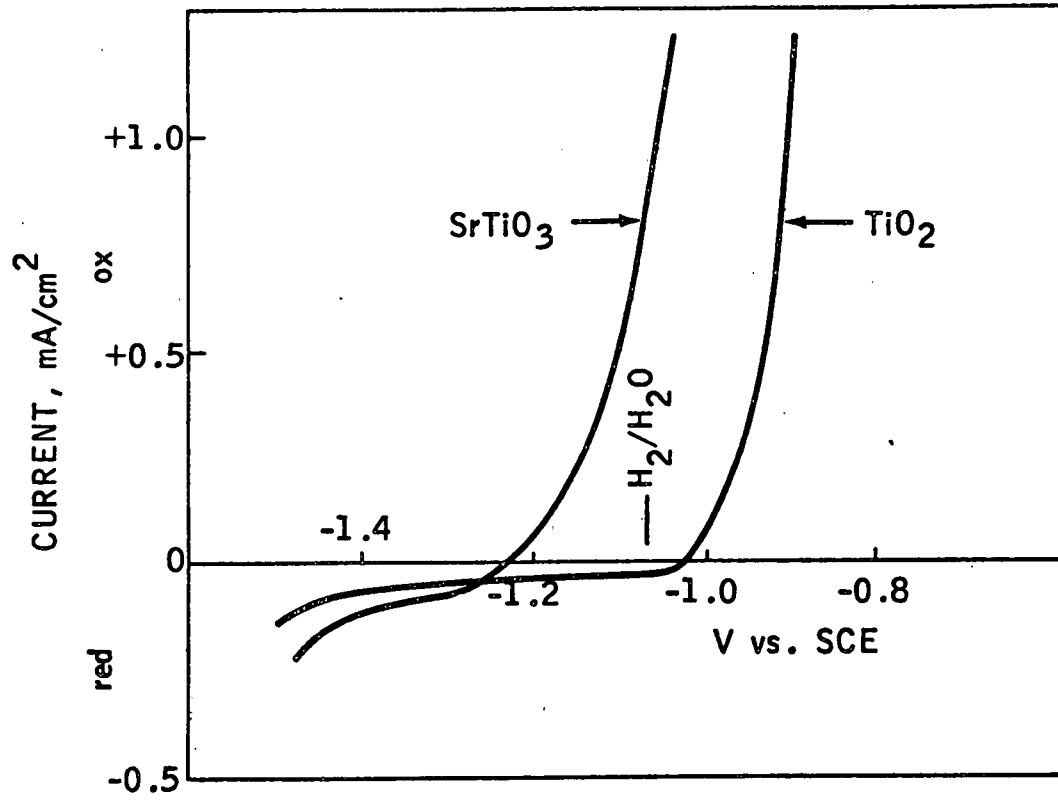
LIST OF FIGURES

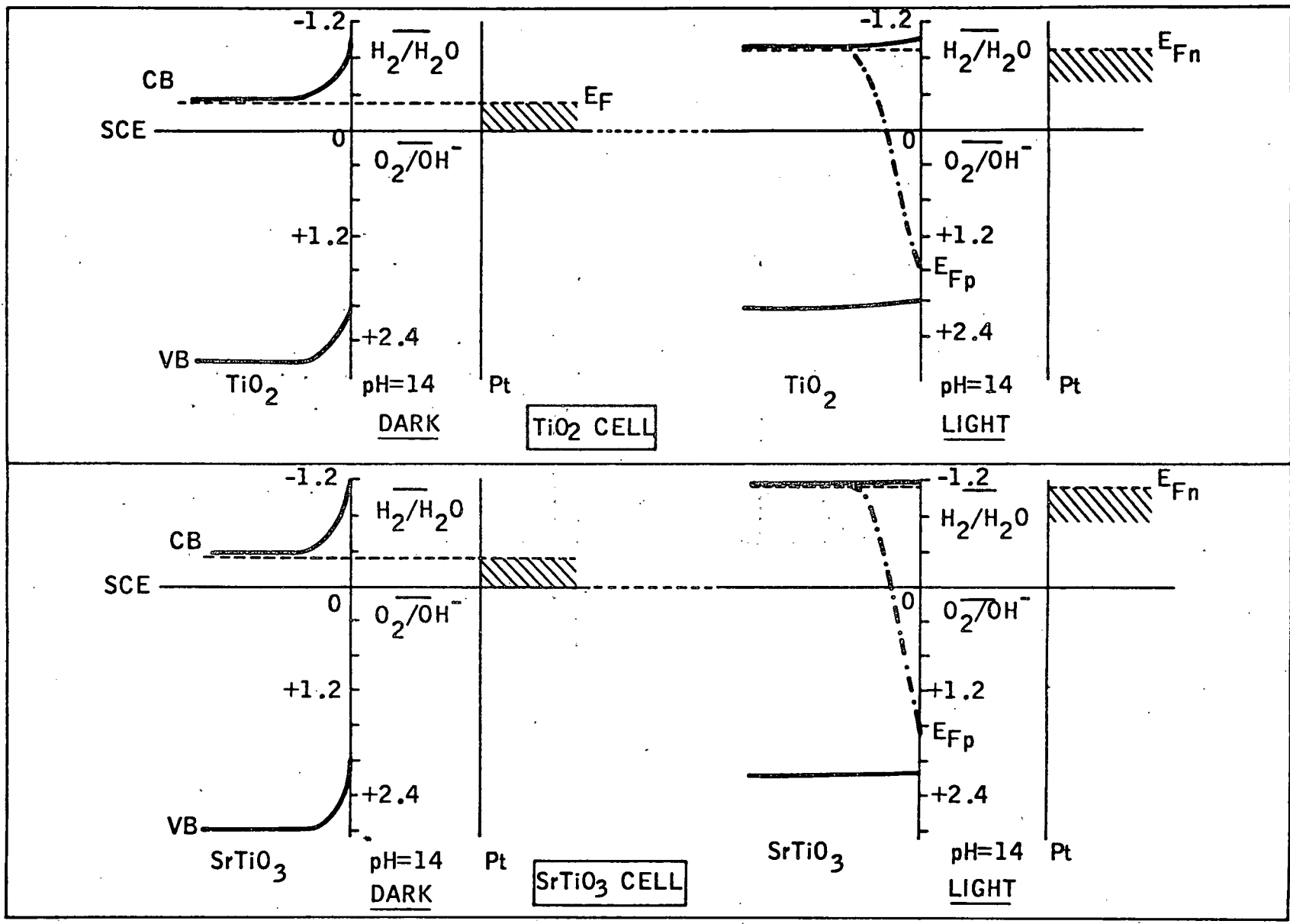
- Figure 1. A Semiconductor electrode in contact with a solution containing a redox couple R/O.
- Figure 2. Current-voltage characteristics of an n-type semiconductor electrode, in the dark and under illumination.
- Figure 3. Typical current-voltage characteristics for an n-type TiO_2 electrode in 5M KOH, both in the dark and illuminated.
- Figure 4. Details of the current-voltage characteristics of illuminated TiO_2 and SrTiO_3 electrodes in the potential region of the $\text{H}_2/\text{H}_2\text{O}$ redox couple (5M KOH solution).
- Figure 5. Energy level diagrams for TiO_2 and SrTiO_3 photoelectrolysis cells in the dark and under illumination.
- Figure 6. Energy relationships for an illuminated semiconductor electrode in contact with a solution.
- Figure 7. Energy relationships in devices using both n- and p-type materials.
- Figure 8. Best fit of experimental quantum efficiency data for undoped and Al-doped TiO_2 to the theoretically developed response curves based on diffusion length and barrier width (Ref. 26).
- Figure 9. Possible absorption processes due to dopant impurities in a material such as TiO_2 ,

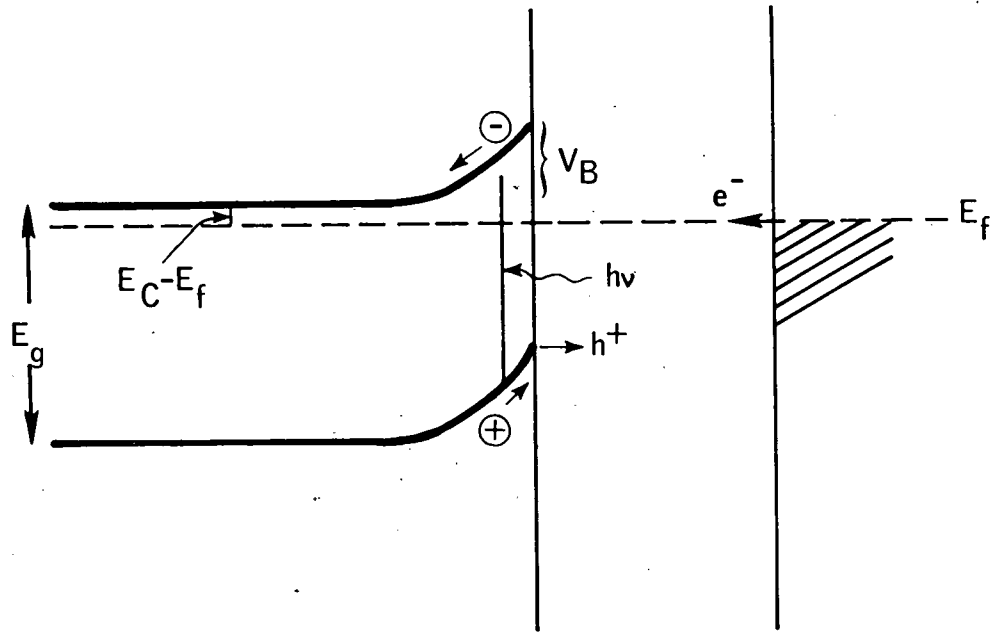


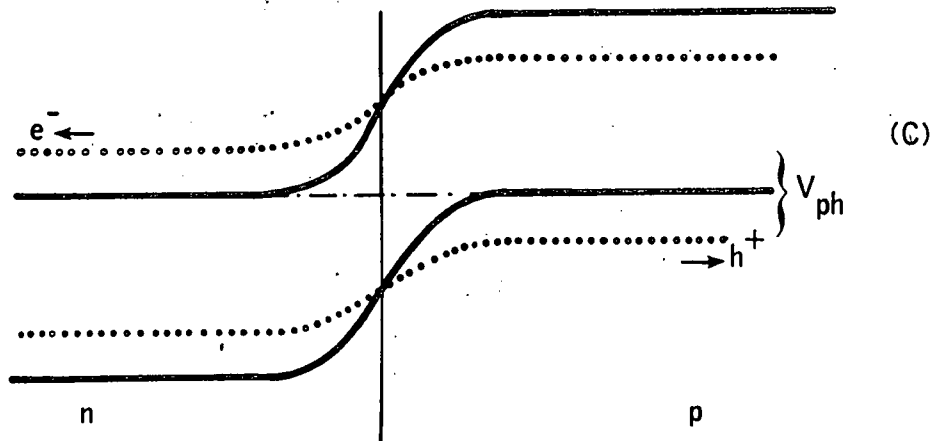
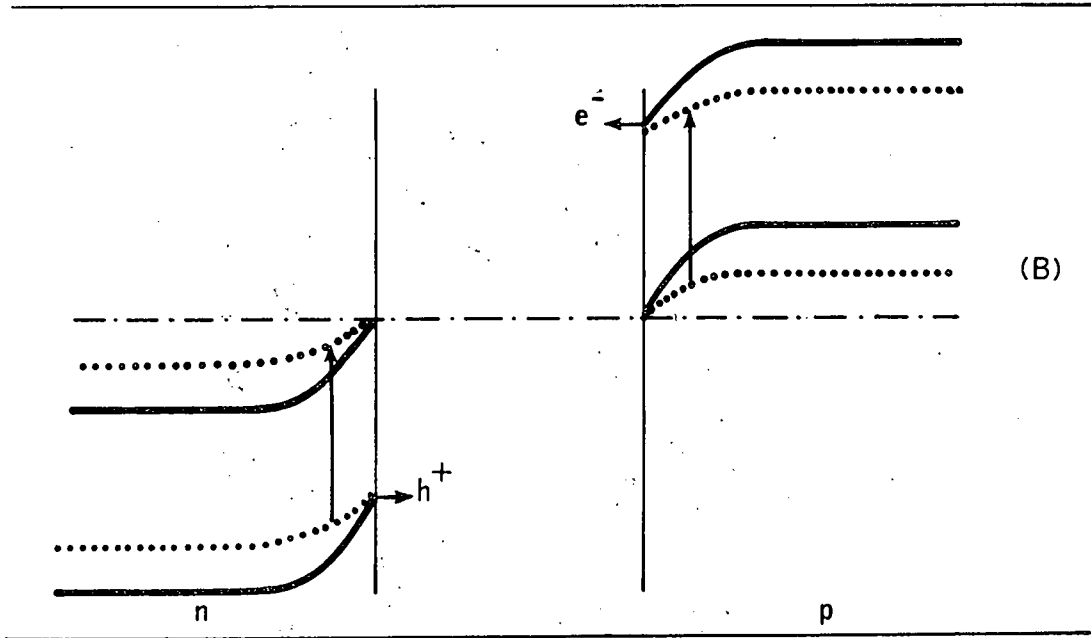
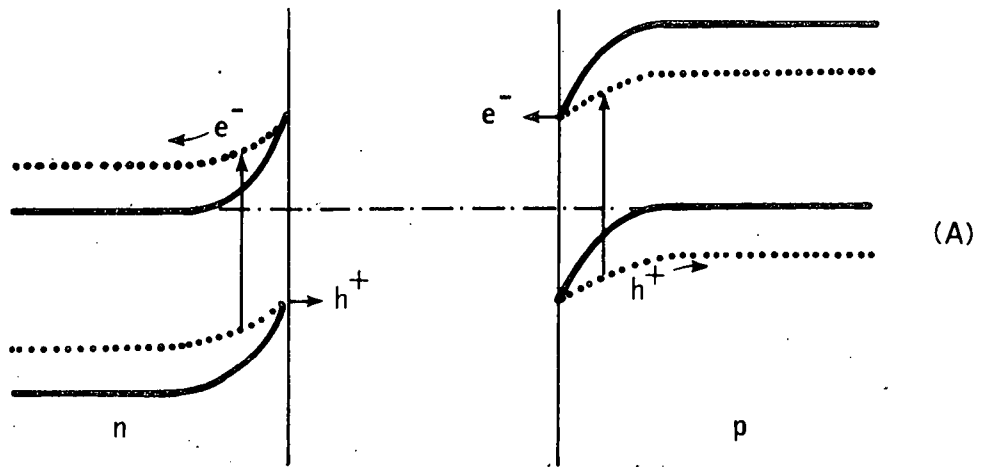


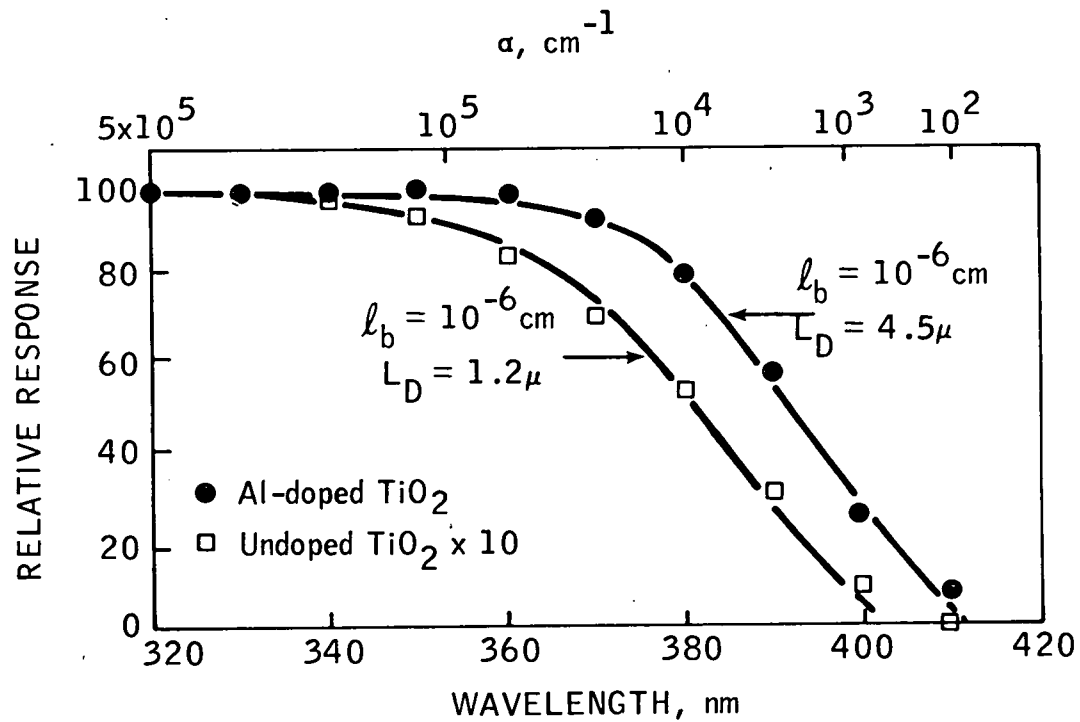


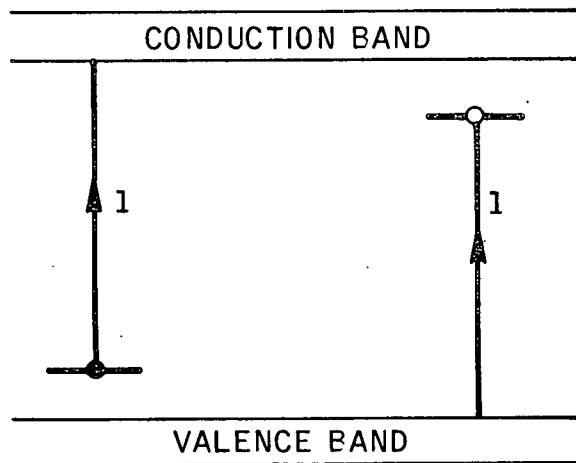
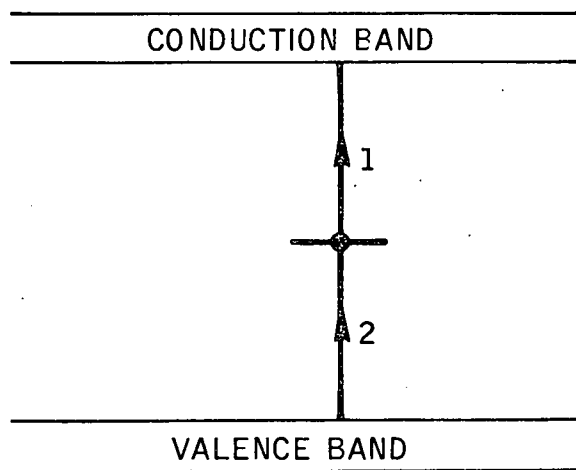
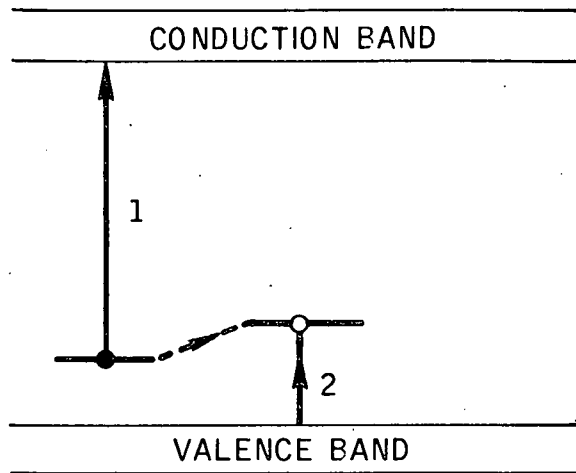












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16. Abstracts The subject of photoelectrolysis of water at illuminated semiconductor electrodes to produce hydrogen is reviewed from 1839 up to the present. 119 literature references are cited. Critical interpretations of important concepts in this area of investigation are given. Techniques for improving the response of cells are discussed, and the expected maximum efficiency is calculated. Additionally, some preliminary experimental results with impurity sensitization of TiO ₂ electrodes and heterostructure formation are presented.			
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