

## PHOTOELECTROCHEMISTRY AND HETEROGENEOUS PHOTOCATALYSIS AT SEMICONDUCTORS\*

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### Summary

The principles and applications of semiconductor electrodes in photoelectrochemical (PEC) cells (liquid junction photovoltaic, photoelectrosynthetic, photocatalytic) are described. Factors important to the design of practical systems and the extension of the principles of PEC cells to particulate systems for carrying out heterogeneous photocatalysis and photosynthesis are discussed. A "dual n-type semiconductor" model of biological photosynthesis is proposed and possible means of utilization of such a system is described.

### 1. Introduction

The conversion of radiant energy to electrical or chemical energy is primarily based upon the intramolecular "pumping" of electrons upon absorption of light in the visible or UV regions to higher energy levels (*i.e.* molecular excitation). Intermolecular electron transfer from these excited molecules, either directly or via an external circuit in an electrochemical cell, provides the basis of the energy conversion process. Efficient utilization of the radiant energy requires separation of the photogenerated electron-hole pairs before recombination, and this has been found to occur quite effectively in the electric field formed at the interface between a semiconductor and an electrolyte solution. This finding has given rise to numerous investigations of the photoelectrochemical (PEC) cells and related systems to be discussed in this paper.

Studies of photoeffects at the semiconductor-liquid interface can be separated into three eras. The earliest work, beginning with the observations

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of Becquerel [1], dealt mainly with the rather small photoeffects observed with metal electrodes (probably covered with thin layers of semiconducting material). The rather extensive work of these times (1839 - 1955) has been reviewed [2, 3]. Extensive investigations of the electrochemistry of the semiconductor materials themselves and photoeffects at these followed, *e.g.* ref. 4. These studies, between 1955 and 1971, by Gerischer, Memming, Williams and others led to models for the semiconductor-liquid interface and provided mechanisms for the electrode reactions which occur there [5 - 8]. Although possible applications to energy conversion were considered rather early [3], real interest in the construction of liquid junction photovoltaic cells and especially in the photoelectrolysis of water at semiconductor electrodes began in about 1971, with the publications of Fujishima and Honda [9]. Reviews of this more recent work and the principles of semiconductor PEC cells have appeared [10 - 13]. In this paper I shall attempt to outline the principles of semiconductor electrode devices, to review the progress in this field to date and to discuss some recent results and ideas from our laboratory in this area.

## 2. Principles of semiconductor electrode PEC cells

Let us consider the formation of the semiconductor-electrolyte solution junction (Fig. 1). Most of the discussion and examples in this paper will deal with n-type semiconductors, since these generally have shown better stability and have been used in most of the reported devices. The principles and applications of p-type materials are generally similar. The Fermi level in the n-type semiconductor before contact with the liquid is located near the energy  $E_c$  of the conduction band edge. The Fermi level in solution is governed by the redox couples present, their concentrations and standard potentials. In Fig. 1 we consider the case where both forms of a redox couple O/R are present (*i.e.* a poised solution), so that the Fermi level in solution is governed by the half-reaction:



When the semiconductor and solution are brought into contact, electron transfer will occur at the interface until the Fermi levels in both phases are equal (this is equivalent to equality of the electrochemical potential  $\bar{\mu}_e$  of the electron in both phases). The situation of interest is that shown in Fig. 1 where  $E_c$  lies above the Fermi level of the redox couple. In this case equilibration occurs by electron transfer from the semiconductor to the solution, causing the semiconductor to become charged positively with respect to the solution. For a moderately doped semiconductor this charge is distributed in a space charge region near the surface of the order of 50 - 2000 Å wide. The electric field produced by this electron transfer is represented by a bending of the bands in the semiconductor in an upward direction (with respect to the bulk semiconductor) and the direction of the field is such that any excess

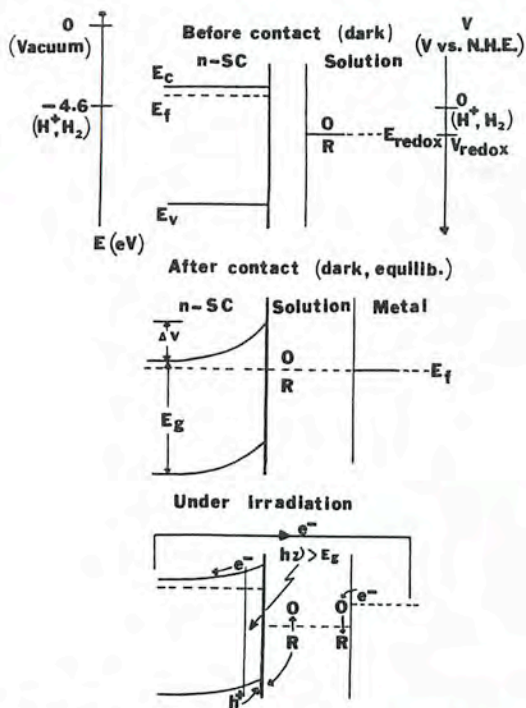


Fig. 1. Representation of the formation of the junction between an n-type semiconductor and solution.

holes created in the space charge region move towards the surface and any excess electrons move towards the bulk. It is this field which provides for efficient hole-electron separation in PEC systems. The charge in the solution for the usual concentrations of electrolytes (greater than 0.1 M) is located very close (less than 10 Å) to the electrode surface. Note that the time for attainment of equilibrium of the semiconductor-liquid interface can be rather long because of slow electron transfer to solution redox levels appreciably below  $E_c$  and also, with some semiconductors, because surface film formation or corrosion of the semiconductor occurs. However, electron transfer in many cases appears to be mediated by surface states or intermediate levels in the gap region and equilibrium is more rapidly attained when the electrode potential is adjusted with a potentiostat or by connection to a poised metallic counter electrode. The condition favorable to hole-electron separation and the production of photocurrents is that illustrated in Fig. 1 where the energy level  $E_{\text{redox}}$  of the redox couple lies below  $E_c$  and the majority carriers (electrons) are depleted in the surface of the semiconductor after electron transfer, *i.e.* a depletion layer forms. If  $E_{\text{redox}}$  is above  $E_c$ , an accumulation layer forms in the semiconductor and the behavior approaches that of a metal-liquid interface.

The electrode potential, which is the usual measured parameter, is denoted here by  $V$  (in volts against the normal hydrogen electrode (NHE)).

The energy levels, denoted by  $E$  (in electron-volts against vacuum), can be related to  $V$  by the equation [6]

$$E_i = \text{constant} - eV_i \quad (2)$$

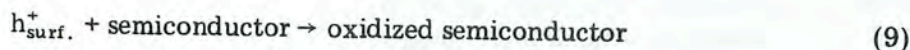
where  $e$  is the electronic charge and the constant has been estimated as  $-4.48$  [14] and  $-4.73$  [15] eV. Thus high  $E_{\text{redox}}$  levels in solution represent couples with negative  $V_{\text{redox}}^{\circ}$  values. The potential corresponding to no excess charge in the semiconductor (*i.e.* the point of zero charge) is called the flat band potential  $V_{\text{fb}}$ . When the semiconductor is at  $V_{\text{fb}}$ , there is no space charge region or electric field in the semiconductor and the bands are flat. Thus the amount of band bending  $\Delta V_{\text{sc}}$  in the semiconductor upon equilibration with a solution redox couple with a potential  $V_{\text{redox}}$  is

$$\Delta V_{\text{sc}} = V_{\text{redox}} - V_{\text{fb}} \quad (3)$$

When light of energy greater than the band gap energy  $E_g$  is absorbed by the semiconductor, electron-hole pairs are generated. Those pairs formed in the space charge region are separated by the electric field. The holes, in the valence band (VB), move to the surface and the electrons, in the conduction band (CB), move into the bulk semiconductor and, in a complete PEC cell, through an external circuit to the counter electrode. Electron-hole pairs generated beyond the space charge region will suffer recombination, except for those that diffuse into that region before recombination occurs. The holes at the surface, delivered at a potential corresponding to the energy  $E_v$  of the VB edge will react with species R causing its oxidation to O; they may also cause oxidation of the semiconductor itself, however. The most negative potential the conduction band electrons can attain is  $V_{\text{fb}}$ . The sequence of reactions that occurs on the absorption of light at the semiconductor-liquid interface can be represented by the equations



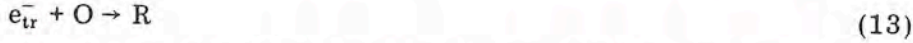
and/or



Loss of efficiency occurs because of recombination of electron-hole pairs at the surface, probably via traps which can accumulate some electrons:



A solution recombination path in which O is reduced by any surface electrons is also possible when the energy level of the trapped electrons lies above  $E_{\text{redox}}$ :



Note that the combination of reactions (8) and (13) is equivalent to the recombination reaction (12).

The design of a practical PEC system demands: (a) high long-term stability of the semiconductor, solution and counter electrode; (b) high efficiency for energy conversion, *i.e.* good quantum efficiency, a good match of  $E_g$  with the solar spectrum and maximum output voltage; (c) inexpensive materials. These requirements can be related primarily to the specific properties of the semiconductor and the solution as follows:

(1)  $E_g$  of the semiconductor should be near that for optimum utilization of solar radiant energy, *i.e.* about 1.1 - 1.3 eV [10].

(2)  $V_{\text{fb}}$  should be as negative as possible (*i.e.*  $E_c$  or  $E_F^{\circ}$  should be as high as possible) to maximize the output voltage and increase the reducing power of the photogenerated electrons.  $V_{\text{fb}}$  primarily depends upon the electron affinity of the semiconductor and the specific adsorption of ions from the solution on the semiconductor surface. Calculations of  $V_{\text{fb}}$  from electronegativity values have recently been described [16].

(3) The semiconductor should be stable in contact with the solution both in the dark and under illumination. The thermodynamic criteria for stabilization of semiconductors based on the relative equilibrium potentials for the decomposition reactions of the material and the redox couple (eqn. (1)) have been discussed [17, 18]. Stabilization can also depend upon kinetic factors, *i.e.* the relative rates of reactions (8) and (9) and the rate of mass transfer of R to the electrode surface. The use of non-aqueous solvents appears to yield improved stability in some cases, especially for small  $E_g$  materials like GaAs and InP [19 - 22].

(4) Polycrystalline materials should be usable and show good efficiencies. Numerous studies of semiconductor-liquid junction cells have shown that polycrystalline materials, produced by a variety of methods (*e.g.* chemical vapor deposition [23, 24], oxidation or anodization of metal substrates [24 - 29], vacuum evaporation [28, 30], electrodeposition [31] and sintering [30, 32, 33]), can be employed and often show efficiencies approaching those of single crystal materials. This is advantageous not only for the ultimate use of inexpensive materials in devices but also because polycrystalline semiconductors can be prepared by relatively simple methods thus providing easy access to new materials and formulations for testing.

(5) The doping level  $N_D$  ( $\text{cm}^{-3}$ ) should be adjusted with respect to the absorption coefficient  $a$  ( $\text{cm}^{-1}$ ) of the semiconductor so that most of the light is absorbed within the space charge region. The thickness  $L_1$  of the space charge or depletion region is given by [5 - 7, 34]

$$L_1 \approx \left( \frac{2\epsilon\epsilon_0}{eN_D} \Delta V \right)^{1/2} \approx \left( 1.1 \times 10^6 \frac{\Delta V}{N_D} \epsilon \right)^{1/2} \approx \frac{1}{a} \quad (14)$$

where  $\Delta V$  is the voltage drop between the electrode surface and the bulk semiconductor or the extent of band bending (in volts) and  $\epsilon$  is the dielectric constant. Thus the doping level should be about

$$N_D = (1.1 \times 10^6) \Delta V \epsilon a^2 \text{ cm}^{-3} \quad (15)$$

A higher doping level will result in loss of quantum efficiency because of bulk recombination (eqn. (7)). A lower donor density will cause the resistance of the semiconductor material to be high, which will result in efficiency losses by  $iR$  drop in the bulk semiconductor and perhaps also because of increased recombination in the space charge region where the field will be decreased. Taking  $\Delta V = 0.5 \text{ V}$ ,  $\epsilon = 10$  and  $a = 10^5 \text{ cm}^{-1}$ , a doping level  $N_D$  of about  $5 \times 10^{16} \text{ cm}^{-3}$  seems appropriate.

(6) The potential of the redox couple should be as positive as possible, consistent with stability of the semiconductor and rapid electron transfer to the VB, to maximize the output voltage. Moreover both forms of the couple, O and R, should be stable in the solvent, be highly soluble, and should not absorb light of energy above or equal to  $E_g$ .

### 3. Types of photoelectrochemical cells

It is convenient to classify PEC cells into three categories: photovoltaic (or regenerative), photoelectrosynthetic and photocatalytic; these are depicted schematically in Fig. 2.

#### 3.1. Photovoltaic cells

In this mode the light which irradiates the semiconductor-solution interface is converted to electricity, ideally with no change in the composition of the solution or the semiconductor material. The driving force for this cell is the underpotential (or "negative overpotential") developed for the oxidation of R to O at the semiconductor. The maximum open circuit voltage  $V_{oc}(\text{max})$  attained by such a cell would be

$$V_{oc}(\text{max}) = V_{redox} - V_{fb} \approx (E_c - E_{redox})/e \quad (16)$$

The maximum "open circuit" efficiency  $\eta_{p,m}(\text{max})$  for monochromatic light of energy  $E_g$  would thus be  $eV_{oc}(\text{max})/E_g$ . The maximum open circuit solar efficiency is given by  $\eta_{p,m}(\text{max}) \eta_{ult}$ , where  $\eta_{ult}$  is the maximum solar efficiency obtainable with a threshold device of energy gap  $E_g$  (see for example Fig. 3 in ref. 10). The variation of the maximum solar efficiency with  $V_{redox} - V_{fb}$  and  $E_g$  is shown in Fig. 3 [30]. The actual efficiency of the cell will be smaller than this because of resistive losses in the semiconductor and solution, overpotentials at the metal counter electrode and a quantum efficiency of charge separation (which depends upon the extent  $\Delta V$  of band bending) less than one. Analyses of the power efficiency of such cells, which generally follow those of solid state photovoltaic devices, have been presented [13, 35, 36]. The earliest cell of this type was that employing

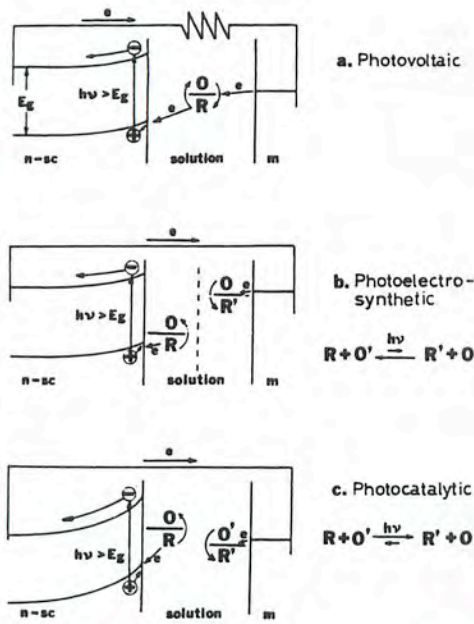


Fig. 2. Schematic representations of different types of photoelectrochemical cells and processes. (a) Photovoltaic cell: e.g. n-TiO<sub>2</sub>/NaOH, O<sub>2</sub>/Pt or n-CdS/S<sup>2-</sup>, S<sub>x</sub><sup>2-</sup>/Pt. (b) Photoelectrosynthetic: e.g. SrTiO<sub>3</sub>/H<sub>2</sub>O/Pt or n-TiO<sub>2</sub>/OH<sup>-</sup>/H<sup>+</sup>/Pt for production of H<sub>2</sub> and O<sub>2</sub>. (c) Photoelectrocatalytic: e.g. n-TiO<sub>2</sub>/CH<sub>3</sub>COOH, CH<sub>3</sub>CN/Pt. Long arrows in reactions represent the spontaneous direction ( $\Delta G^\circ < 0$ ). Although cells shown are for n-type semiconductors, equivalent cells for p-type semiconductors have also been formulated [61].

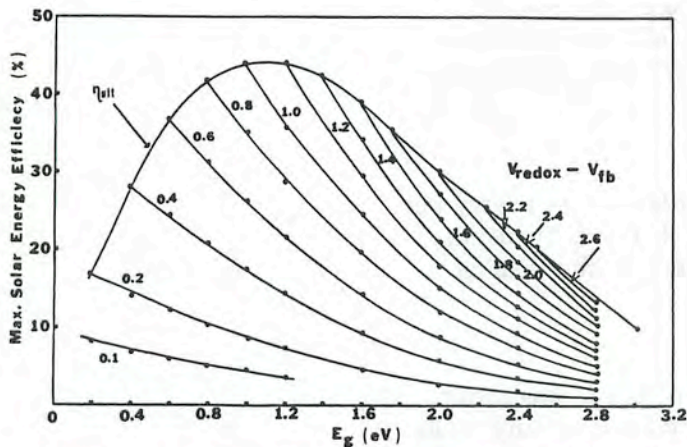


Fig. 3. Maximum thermodynamic open circuit solar efficiencies (AM 1 sunlight) for liquid junction photovoltaic cells with various values of  $E_g$  and  $V_{redox} - V_{fb}$  [30].

n-TiO<sub>2</sub> and the O<sub>2</sub>/H<sub>2</sub>O redox couple. A cell with a cathode of the fuel cell type (Pt-C-Teflon) (where air or oxygen was reduced) and a polycrystalline (chemically vapor deposited) TiO<sub>2</sub> photoanode (where water was oxidized)

operating in acidic or alkaline electrolytes was described by Laser and Bard [37]. This cell had an open circuit voltage of 0.89 V and showed a maximum (monochromatic light) power efficiency of about 1 - 2%. Similar cells using the smaller band gap material n-type  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and the O<sub>2</sub>/H<sub>2</sub>O or I<sub>2</sub>/I<sup>-</sup> couples have also been described [24]. The most successful cells of this type have employed the S<sup>2-</sup>/S<sub>x</sub><sup>2-</sup> and Se<sup>2-</sup>/Se<sub>2</sub><sup>2-</sup> redox couples with n-CdX (X = S, Se, Te) or n-GaAs semiconductor photoanodes [26, 27, 30 - 32, 38 - 42]. For example, the cell n-GaAs (single crystal)/0.8 M K<sub>2</sub>Se, 0.1 M K<sub>2</sub>Se<sub>2</sub>, 1 M KOH/C had a solar energy efficiency of about 9% and showed good long term stability [43].

### 3.2. Photoelectrosynthetic cells

In these cells (Fig. 2(b)) light is used to drive the overall cell reaction in a non-spontaneous direction ( $\Delta G > 0$ ) so that radiant energy is stored as chemical energy (e.g. in fuels). Although the production of H<sub>2</sub> and O<sub>2</sub> by decomposition of water is a major goal of this research, it has been difficult to accomplish this in an unbiased semiconductor PEC cell with a good efficiency. The semiconductor required for such a cell must have a  $V_{fb}$  more negative than  $V_{redox}$  of the H<sup>+</sup>/H<sub>2</sub> couple in the appropriate medium plus any overpotential ( $\eta_{H_2}$ ) required to drive the hydrogen evolution reaction at the counter electrode, i.e.  $V_{fb} \leq -0.059 \text{ pH} - \eta_{H_2}$  V vs. the NHE. It must also be stable with respect to photooxidation while evolving O<sub>2</sub>. Cells employing n-SrTiO<sub>3</sub> ( $E_g = 3.2$  eV) [44 - 46], n-KTaO<sub>3</sub> ( $E_g = 3.4$  eV) [47] and KTa<sub>0.77</sub>Nb<sub>0.23</sub>O<sub>3</sub> ( $E_g = 3.2$  eV) [47] appear to be capable of causing the photodecomposition of water when connected to a Pt counter electrode without an external bias but the efficiencies under these conditions, even with monochromatic light of energy greater than  $E_g$ , are very low. The application of an external bias to the cells improves the efficiency because the extent of band bending is increased improving the efficiency of electron-hole pair separation. The efficiency of the cell can be defined as [44]

$$\eta = (1.23(\text{eV})\Phi - V_{\text{appl}}e)/E_{\text{irr}} \quad (17)$$

where  $V_{\text{appl}}$  is the applied bias in volts, 1.23 eV represents the free energy per electron for the reaction of the resulting H<sub>2</sub> with O<sub>2</sub>,  $\Phi$  is the quantum efficiency for electron flow and  $E_{\text{irr}} (\geq E_g)$  is the energy of the light in electron-volts. The maximum efficiency for the cell

n-SrTiO<sub>2</sub> (single crystal)/9.5 M NaOH/Pt

irradiated with 330 nm (3.76 eV) light with  $V_{\text{appl}} = 0.25 - 0.4$  V was about 20% [44]. The solar efficiency of such a cell would, of course, be tiny. Cells employing n-TiO<sub>2</sub> ( $E_g = 3.0$  eV), when biased either externally or internally (by using an acidic electrolyte at the Pt cathode and a basic electrolyte at the TiO<sub>2</sub> anode in a divided cell arrangement), can be used to produce H<sub>2</sub> under solar irradiation [48, 49]. The monochromatic efficiencies of these cells are of the order of 1 - 2%. In addition to production of H<sub>2</sub> and O<sub>2</sub> other reactions of chemical interest can be driven in a photoelectrosynthetic cell. For



example the oxidation of  $\text{Br}^-$  (at polycrystalline  $\text{n-TiO}_2$ ) to form bromine (which could then react with organics, *e.g.* aniline) with  $\text{O}_2$  reduction occurring at the Pt counter electrode was described [50]. The photo-assisted oxidations of  $\text{Cl}^-$ ,  $\text{Ce}^{3+}$  and  $\text{Mn}^{2+}$  at  $\text{n-TiO}_2$  have also been demonstrated [50, 51]. In photoelectrosynthetic cells either the (spontaneous) back reaction of the products  $\text{R}'$  and  $\text{O}$  must be very slow or they must be separated by using a membrane or diaphragm in the PEC cell. This situation may place limitations on the use of powder or particulate systems for carrying out heterogeneous photosynthesis, as discussed later.

### 3.3. Photocatalytic cells

In these cells (Fig. 2(c)) a reaction is driven in a spontaneous ( $\Delta G < 0$ ) direction by the light energy. Here radiant energy is not converted to chemical energy but is used to overcome the energy of activation of the process. Thus cells employing  $\text{n-TiO}_2$  electrodes have been used to carry out the oxidation of  $\text{CN}^-$  [50], acetate (to ethane and  $\text{CO}_2$ ) [52],  $\text{I}^-$  [50, 51], alcohols and a number of organic species [50, 53 - 55]. These cells, or the heterogeneous photocatalytic systems derived from these described later, are useful in carrying out chemical reactions (*e.g.* decarboxylation of acids in the "photo-Kolbe reaction" [52]) and perhaps for large scale processes, such as water or waste treatment. They may also be considered as photoactivated fuel cells, in which a waste product such as acetate or another material derivable from the biomass is photooxidized at an n-type semiconductor anode in a cell with a conventional oxygen cathode. Mixing of products  $\text{R}'$  and  $\text{O}$  is not a problem in these systems. Studies of photoelectrosynthetic and photocatalytic reactions are also of interest because they provide information about the factors which govern competitive reaction paths for photogenerated holes. Thus it has been found that many compounds can compete successfully with water for the holes and high current efficiencies for the photo-oxidations (*e.g.* 60 - 80% for  $\text{I}^-$  oxidation) are observed. The trend observed appears to show that the current efficiency increases with the  $V_{\text{redox}}^\circ$  of the couple and this has been ascribed to the participation of energy states within the band gap region in the electron transfer process [50, 51]. An understanding of competitive reaction rates is clearly of importance in the stabilization of semiconductors with respect to photodecomposition by addition of suitable redox couples in photovoltaic cells.

## 4. Heterogeneous photosynthesis and photocatalysis at powders

The principles of photoelectrosynthetic and photocatalytic semiconductor cells can be extended to the design of particulate systems for carrying out the desired reactions. For example (Fig. 4) a particle of  $\text{TiO}_2$  with some Pt deposited on it can be thought of as a short-circuited PEC cell (*e.g.* Fig. 2(c)) where the desired overall reaction occurs by electron and hole transfer at two sites on the particle. These particulate systems have the

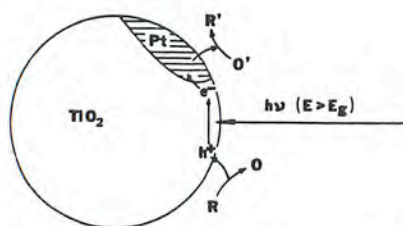


Fig. 4. Schematic representation of a photocatalytic reaction on a platinized semiconductor powder particle.

advantage compared with PEC cells of being much simpler and less expensive to construct and use. Moreover the efficiency of light absorption in suspensions or slurries of the powders can be very high. Finally a variety of materials can be used in particulate systems which may not be available as single crystal or even polycrystalline semiconductor electrodes for example, because their electrical resistivity is too high or because they cannot be fabricated into electrodes. By analogy with the PEC cells, two types of heterogeneous photosystems can be defined. In "heterogeneous photosynthesis" a thermodynamically unfavorable reaction ( $\Delta G > 0$ ) is caused to occur by the presence of an illuminated solid, with the conversion of radiant to chemical energy. In "heterogeneous photocatalysis" the rate of a thermodynamically favorable reaction ( $\Delta G < 0$ ) is increased by the presence of the illuminated solid [56]. It is a requirement in both types of photoprocesses that the solid (catalyst) itself is not consumed. Most studies of semiconductor heterogeneous photocatalysis have been concerned with gas phase reactions [57]. Studies of solution processes have been less frequent and have been to a large extent concerned with the synthesis of  $\text{H}_2\text{O}_2$  by reduction of oxygen by a reductant (e.g. oxalate or formate) in the presence of  $\text{ZnO}$  or another semiconductor [58]. A review of past research in this area and a discussion of the principles of relating electrochemical measurements to photocatalytic behavior has appeared [56].

A number of types of particulate systems can be envisaged (Fig. 5). (a) A single powder may provide both the oxidizing and reducing sites for the reaction. Thus undoped anatase ( $\text{TiO}_2$ ) has been used for the photocatalytic oxidation of  $\text{CN}^-$ , with concomitant reduction of  $\text{O}_2$  [59, 60]. With an n-type powder photooxidation occurs and the reduction is the "dark site" reaction. The converse is true with a p-type powder. (b) Because the dark site reactions may not occur with as high an efficiency (e.g. with as low an overpotential) as on a metallic or electrocatalytic site, higher efficiencies may be obtained by modifying a portion of the powder surface by deposition of metal (or electrocatalyst). Thus platinized anatase has been shown to be more effective in the photodecarboxylation of acetate compared with anatase alone [61]. This metallization of the semiconductor can sometimes be carried out by a photocatalytic process, as described below. (c) The p-n powder requires two photons for the overall reaction; the photooxidation

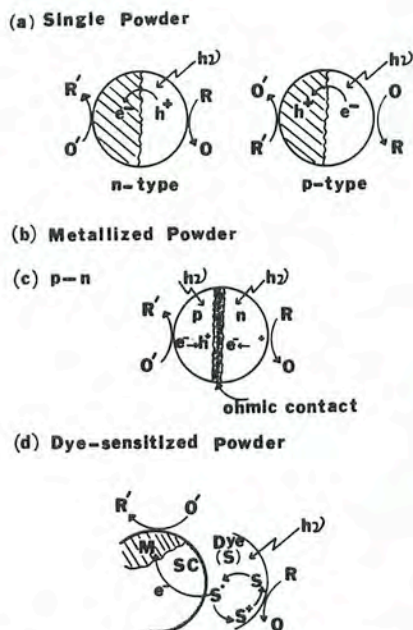


Fig. 5. Different configurations of particulate semiconductor systems for carrying out photosynthesis and photocatalysis. (a) Single powder (shaded area represents dark side of powder); (b) metallized powder (as (a), except shaded area represents deposited metal); (c) p-n powder; (d) dye sensitized powder.

occurs at the n-type material and the photoreduction occurs at the p-type. Such devices have been called photochemical diodes [62] and, although actual polycrystalline particulate materials such as these have not been described, a structure of this type has been produced by bonding together metallized single crystals of n-TiO<sub>2</sub> and p-GaP with silver epoxy cement. The junction between the p- and n-materials must be ohmic for the particles to work as described. (d) The particles can also be coated with a dye which can act as a sensitizer and extend the response to wavelengths corresponding to energies below  $E_g$ . Particulate systems involving dye sensitization would have the important advantage compared with sensitized semiconductor electrodes in PEC cells of having enhanced efficiency for light absorption even for thin layers of dye and of suffering less from resistance effects in multilayers of the dyes. Although there has been extensive research on dye sensitized semiconductor electrodes [6, 12, 63], particulate systems have not been described.

A number of applications of these particulate systems can be envisaged and several of these have been put into practice. The examples here will mainly stress the results from our laboratory. (1) The photocatalytic oxidation of cyanide, sulfide and other pollutants can be carried out on n-TiO<sub>2</sub>, n-ZnO and n-CdS [59, 60]. The cathodic process in these reactions is the reduction of oxygen. Rates of CN<sup>-</sup> removal under unfocused solar irradiation

of  $3.1 \mu\text{mol d}^{-1} \text{cm}^{-2}$  from a solution containing 30 mM KCN and 0.1 M KOH have been reported. Even at this rate practical applications appear feasible. (2) The photocatalytic oxidative decarboxylation of acetate and other carboxylates occurs at both single powder and platinized n-TiO<sub>2</sub> [61]. While the reaction of acetate at n-TiO<sub>2</sub> in a PEC cell leads mainly to ethane via the path [52]

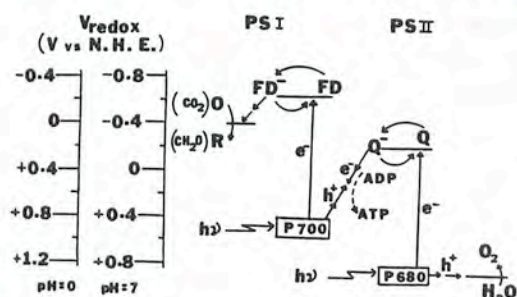


the heterogeneous photocatalytic process produces mostly methane [61]. This has been ascribed to the relatively low light flux on the large area powders decreasing the surface concentration of methyl radicals and thus the contribution of the coupling reaction, as well as the production of these radicals near reductive sites on the same particle where reduction either directly or via an H atom can occur. The existence of methyl radical intermediates in this process has recently been demonstrated by electron spin resonance spectroscopy using spin trapping with  $\alpha$ -phenyl-N-tert-butyl nitron [64]. Spin trapping techniques have also been applied recently to demonstrate the formation of O<sub>2</sub><sup>-</sup> during irradiation of a CdS suspension [65]. (3) The photodeposition of some metals on semiconductor powders occurs under irradiation. Thus irradiation of anatase powder suspended in an acetic acid medium containing chloroplatinic acid produced platinized TiO<sub>2</sub> with the evolution of CO<sub>2</sub> [66]. This material was used as the photocatalyst in the decarboxylation reactions and could also be used as a conventional catalyst for the hydrogenation of benzene [67]. Deposition of copper from dilute solutions (about  $4.2 \mu\text{g Cu ml}^{-1}$ ) on n-TiO<sub>2</sub> and n-WO<sub>3</sub> under xenon lamp and solar irradiation has also been accomplished recently [68]. Note again that the use of particulate systems follows closely the results on metal deposition found in PEC cells [69, 70]. The requirement for metal deposition at the n-type semiconductor is that  $V_{M^{+n}/M} > V_{fb}$  (where  $V_{M^{+n}/M}$  is the thermodynamic potential under the given solution conditions) and that some suitable irreversible oxidation process is available. (4) Polymerizations can also be initiated by a photocatalytic process. Thus methyl radicals or other species photogenerated at platinized TiO<sub>2</sub> can initiate polymerization of methylmethacrylate and other monomers [71]. (5) True photoelectrosynthesis at particulate semiconductors has been the subject of relatively few studies. The photooxidation of water by Fe<sup>3+</sup> and quinone in the presence of ZnO, TiO<sub>2</sub> and WO<sub>3</sub> has been reported [56] and formation of H<sub>2</sub> and O<sub>2</sub> upon irradiation of platinized TiO<sub>2</sub> (rutile) in 1 N H<sub>2</sub>SO<sub>4</sub> has been claimed [72]. A prime difficulty with heterogeneous photosynthesis is that the reduced and oxidized intermediates or products which are capable of reacting with each other are produced in close proximity on a particle. This back reaction leads to low efficiency of the overall process as does "short circuiting" of the process by the product formed at an oxidizing site being reduced back to starting material at the neighboring reducing site. For example the system n-CdS (single crystal)/Pt in 1 M Na<sub>2</sub>S-1 M NaOH was

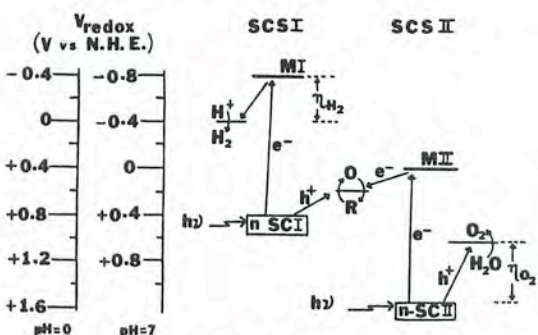
reported to evolve  $H_2$  with the concomitant oxidation of  $S^{2-}$  to  $S_x^{2-}$  under irradiation [62]. Hydrogen evolution, however, would probably not continue in this system, because with the build-up of  $S_x^{2-}$  this species would be preferentially reduced at the Pt. Thus heterogeneous photosynthesis would probably be most efficient where the generated intermediates react very rapidly and irreversibly to form products that will leave the particle site.

## 5. Semiconductor model of photosynthesis

In many ways the utilization of semiconductor systems for photoelectrosynthesis resembles the biological photosynthetic system in plants, and indeed parallels between the two have been drawn [9, 35, 73]. A simplified representation of the redox processes, electron transport and redox potentials in biological photosynthesis is given in Fig. 6(a). This process carries out the oxidation of water and the reduction of  $CO_2$ , a reaction which requires thermodynamically about 1.23 eV (118 kJ per electron) by the absorption of two photons per electron transported through the chain. This is accomplished by two photosystems (PS I and PS II) in which the reaction centers, which are two different chlorophyll-protein com-



(a) Biological Photosynthesis



(b) Semiconductor Photoelectrosynthesis

Fig. 6. Comparison of (a) biological photosynthesis and (b) dual n-type semiconductor model, representing the electron transport chain and redox potentials.

plexes (designated P700 and P680), are excited and in both cases deliver an electron to a suitable acceptor molecule. The oxidized center in PS II ultimately causes the oxidation of water, while the oxidized center in PS I is reduced by an electron originating in PS II. While the previous semiconductor analogies to biological photosynthesis employed either a single n-type semiconductor [9, 73] or a p-n pair [35], it is clear that a closer analogy is a pair of n-type semiconductor systems (SCS I and SCS II) (Fig. 6(b)). Examination of the conditions needed to photoelectrolyze water with efficient utilization of solar energy and taking account of the energies of activation (*i.e.* overpotentials) required allow the desired properties of the semiconductors and solution to be deduced. The intermediate couple O, R plays the role of transferring an electron between the two systems and could serve to stabilize semiconductor I. Oxygen is evolved at semiconductor II (by analogy with PS II) and hydrogen is evolved at the counter electrode in SCS I. Semiconductor I should have  $V_{fb}$  sufficiently negative for  $H_2$  production including a reasonable overpotential  $\eta_{H_2}$  for evolution at the counter electrode (M I) (assumed to be  $-0.4$  V). Thus for SC I,  $V_{fb} \leq -0.4 - 0.06$  pH V *vs.* the NHE. For efficient utilization of solar energy,  $E_g \approx 1.2$  eV. The location of the valence band edge of semiconductor II must be sufficiently positive to cause water oxidation, again assuming a needed overpotential  $\eta_{O_2}$  of 0.4 V. Thus, taking  $E_g$  for SC II as 1.2 eV,  $V_{fb} \geq +0.4 - 0.06$  pH V *vs.* the NHE; SC II must also be stable with respect to photodecomposition when oxygen is evolved at its surface. These values place  $V_{redox}$  for system O/R at  $+0.6 - 0.06$  pH, which allows 0.2 V overpotential for both the

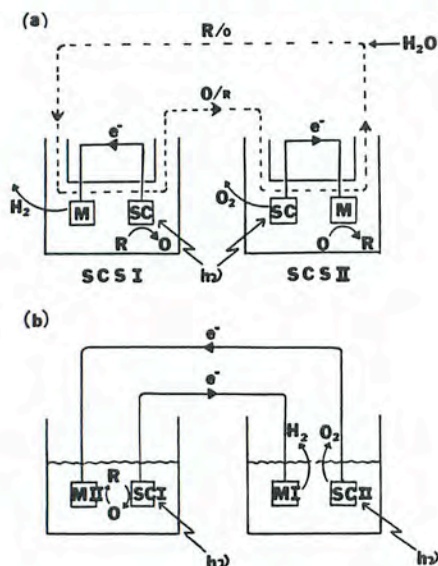


Fig. 7. Cell configurations for carrying out photoelectrosynthetic production of hydrogen and oxygen from water using dual n-type semiconductor system. (a) Direct system with circulating electrolyte. (b) Equivalent system with photoelectrosynthetic cell biased by a photovoltaic cell.

oxidation and reduction reactions for this couple. Larger overpotentials can be obtained, of course, by increasing  $E_g$  of the semiconductors. While formally this system resembles photosynthesis and it is interesting that the potential levels arrived at in the semiconductor system by considering the thermodynamics and kinetics of the reactions are very close to those in the biological system (compare Figs. 6(a) and 6(b)), practical difficulties exist in actually constructing such a system as depicted (Fig. 7(a)). The intermediate O must react slowly with  $H_2$  and must not be brought at high concentration to M I, since it will be preferentially reduced. Similarly R must react slowly with oxygen and should not reach SC II in high concentration. These requirements may be difficult to attain while maintaining high efficiency and stability. Different configurations of equivalent cell systems, *e.g.* by adding membranes or separators, are possible. One such equivalent system is shown in Fig. 7(b). Here the photovoltaic cell (SC I/O, R/M II) provides the additional bias needed to operate the photoelectrosynthetic cell producing hydrogen and oxygen (M I/ $H_2O$ /SC II). A particulate system based on this dual n-type semiconductor arrangement, *e.g.* with circulation through two packed or fluidized beds, would be highly desirable but would probably have serious problems with short circuiting reactions ( $O \rightleftharpoons R$ ) on the particles.

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