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Photoelectrochemistry

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Summary. The electron-hole pair formation that occurs at the interface between a semiconductor and a solution upon absorption of light leads to oxidation or reduction reactions of solution species. The principles of such photodriven processes are described as well as applications of semiconductors in electrochemical cells and as particulate systems for carrying out heterogeneous photocatalysis and photoelectrosynthesis.

The interconversion of different forms of energy has been of central importance in science and technology. Just as the practical application of heat engines, electric generators and motors, and storage batteries led to the development of the fields of thermodynamics and electrochemistry in the 19th and 20th centuries, so the problem of utilizing solar energy for the direct production of electricity and fuel has become a field of much current interest and has encouraged new fundamental investigations of the interactions of light, electron flow, and chemical reactions at electrode surfaces in electrochemical cells.

Sunlight in the near infrared, visible, and near ultraviolet regions has considerable energy (about 0.9 to 3.2 electron volts per photon, or about 87 to 308 kilojoules per mole) and intensity and could provide a significant contribution to our electrical and chemical resources if efficient and inexpensive systems utilizing readily available materials could be devised for the conversion process. Indeed the fossil fuels we largely depend on for our current energy needs presumably originated from biological photosynthesis, and even now the burning of wood represents an important part of the world energy supply. However, biological photosynthesis is relatively inefficient in terms of conversion of solar energy to dry fuels, with overall field efficiencies of about 1 percent (*1*). The fabrication of artificial photosynthetic systems for the conversion of abundant materials (for example, H_2O and CO_2) to fuels (for example, H_2 and CH_3OH), directly or by electrolysis or the production of electricity, is clearly an important goal (*2, 3*). Moreover, photochemical reactions could be employed to replace other energy-consuming chemical processes, for example, for pollution abatement or in chemical synthesis. One of the more promising approaches to the design of such systems involves the application of photoelectrochemical cells or powder catalysts made of semiconductor materials. In this article I describe the basic principles of such systems, review some of their applications, and touch briefly on the relevancy of the concepts developed for these systems to such diverse topics as photography, electrochromic displays, and chemical evolution.

Basic Principles

The conversion of light to electrical or chemical (redox) energy results from light in the visible region acting as an electron pump. The absorption of a photon by an atom or molecule pumps an electron from a lower orbital to a higher one (Fig. 1A). The wavelength of light that causes such a transition is that with an energy equal to or greater than the difference in energies of the two orbitals, E_g. The result is an electron-hole (e^-h^+) pair formed by this intramolecular pumping in species, S. This produces an excited state, denoted S* (see Fig. 1A). If the e^-h^+ pair can be separated so that the e^- flows to a suitable acceptor species, A,

$$S^* + A \rightarrow S^+ + A^- \qquad (1)$$

or an electron from a suitable donor, D, fills h^+

$$S^* + D \rightarrow S^- + D^+ \qquad (2)$$

then the light energy has been stored, at least for a short time, as redox chemical energy. The reaction of S^+ and A^- or S^- and D^+ is spontaneous (or "downhill") and capable of liberating energy (that is, is exoergic). If e^- is pumped through a wire, it has been converted to an electrical current flow. However, excited states are very short-lived (typically lasting from nanoseconds to milliseconds in liquids) and the e^-h^+ pairs frequently recombine very quickly with the captured light energy degraded to heat or, sometimes with the emission of a photon, as in phosphorescence. To utilize the light in a form other than heat, one must achieve separation of the e^-h^+ pair before recombination. This separation can be promoted by an electric field (that is, a difference in electrical potential) or a "chemical field" (that is, a difference in chemical potential, as occurs in the presence of A or D). Unless the back reaction between S^+ and A^- or between S^- and D^+ is slow, the back electron transfer to produce S and A or S and D, respectively, will occur very quickly, and again this immediate intermolecular e^-h^+ recombination will usually result in heat production. If the chemical energy is to be stored in the form of oxidized and reduced species, either the energy of activation for this recombination process must be high, so that the back reaction is slow, or the oxidized and reduced products must have been formed at some dis-

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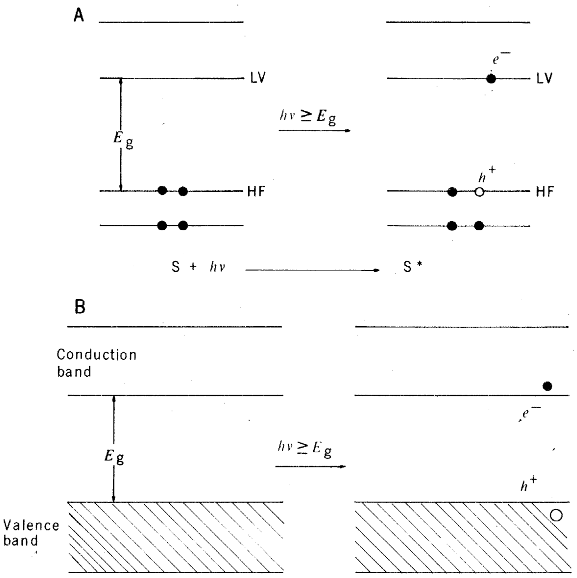


Fig. 1. (A) Electronic orbitals and light absorption in an atom or molecule, S. (B) Semiconductor bands and electron-hole pair formation on light absorption.

tance from one another so that they can be separated before reacting.

Light absorption occurs in a similar way in a semiconductor (Fig. 1B). In semiconductors (for example, silicon, titanium dioxide, cadmium sulfide, gallium arsenide, and a wide range of other inorganic, organometallic, and organic substances) the orbitals are merged into a nearly filled valence band and a nearly vacant conduction band separated by the energy gap, E_g. When a semiconductor is immersed in a solution, charge transfer occurs at the interface because of the difference in the tendency of the two phases to gain or lose electrons (that is, difference in electron affinity or electrochemical potential of the two phases). The net result is the formation of an electrical field at the surface of the semiconductor to a depth of 5 to 200 nanometers. The direction of this electric field depends on the relative electron affinities of the semiconductors and solution. For an n-type semiconductor, which is one that is doped with a donor species so that some electrons are in the conduction band, the field frequently forms in the direction from the bulk of the semiconductor toward the interface (Fig. 2A). Thus, if an e^-h^+ pair forms in this region of the semiconductor (the space charge region) because light is absorbed at the interface, the electron moves toward the bulk of the semiconductor and the hole moves toward the surface. Thus the electric field that forms spontaneously at the interface accomplishes the e^-h^+ separation. The electric field within the semiconductor is represented, as in Fig. 2A, by a bending of the bands. In such diagrams, where the energy levels represent electronic energy, electrons move spontaneously "downhill" and holes, "uphill." After separation, what is the fate of e^- and h^+? If the solution contains a species, D, which has an energy level (that is, a solution redox potential) above that of the photogenerated hole at the surface, the electron transfer reaction

$$\mathrm{D} + h^+ \rightarrow \mathrm{D}^+ \qquad (3)$$

can occur. The excited electron, which can have an energy approaching that of the conduction band edge, can be transferred through a wire connected to the semiconductor to a second, nonphotoactive electrode (for example, made of carbon or a metal) where some oxidized form, O, can be reduced

$$\mathrm{O} + e^- \rightarrow \mathrm{R} \qquad (4)$$

The combination of the n-type semiconductor and the inert electrode immersed in the electrolyte solution comprises a photoelectrochemical cell (Fig. 2, B and C) in which light promotes the overall reaction

$$\mathrm{O} + \mathrm{D} \rightarrow \mathrm{R} + \mathrm{D}^+ \qquad (5)$$

For example, if O and D were both water, Eq. 5 would represent the photodecomposition of the water to H_2 and O_2

$$2H_2O \rightarrow O_2 + 2H_2 \qquad (6)$$

Although this interesting and potentially useful reaction has been demonstrated in such photoelectrochemical cells, its efficiency with the semiconductor materials employed so far (for example, TiO_2 and $SrTiO_3$) has been too low, for light that is characteristic of the solar spectrum, to be of practical interest. The reaction in Eq. 5 could be carried out by conventional electrochemical methods in cells such as those used to electrolyze water or to produce chlorine; in these an external electrical source drives the reaction in the uphill direction. In the photoelectrochemical cell it is light that pumps the electrons and provides the needed energy. Note that the photoelectrochemical cell provides both the required field for e^-h^+ separation as well as the considerable spacial separation of the products R and D^+ which are potentially capable of reacting with one another.

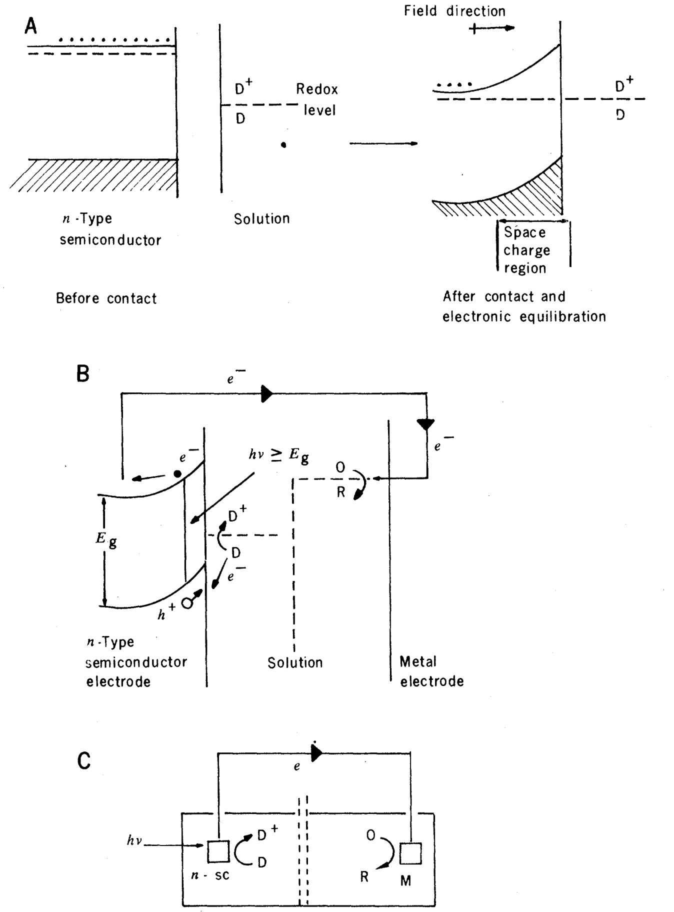
Cells constructed with p-type semiconductors can be described in a similar way (Fig. 3). A p-type semiconductor is one that is doped with an acceptor impurity to produce holes in the valence band. When a p-type material contacts a solution with a redox couple at an energy within the band gap of the semiconductor (Fig. 3A), electronic equilibration again produces a space charge region with the field now pointing toward the bulk semiconductor. Photogenerated e^-h^+ pairs in the space charge region will again separate; in this case electrons move to the interface, where an acceptor species in solution, A, can be reduced, while holes move to the interior of the semiconductor (Fig. 3, B and C). Therefore, light promotes photoreductions at p-type materials and photooxidations at n-type ones.

This separation of the e^-h^+ pair in the electric field at the semiconductor-solution interface is very similar to that which occurs at the p-n junction of solid-state photovoltaic cells (for example, of Si or GaAs), which are the familiar solar cells used in space and some terrestrial applications. However, several important differences should be noted. Although the solid-state cells pump electrons through an external circuit, no actual chemistry occurs. In the liquid junction cells, since electrons and holes themselves are usually not very stable in the solution medium, their transport through the liquid phase depends on the occurrence of redox reactions at the electrode surfaces. This provides a means of direct conversion of radiant energy to storable chemicals. The occurrence of chemical reactions at the electrode surface also implies the possibility of the semiconductor itself reacting. Thus photogenerated holes produced at an n-type semiconductor may cause oxidation of the semiconductor surface, producing a blocking layer or dissolution of the electrode, as well as the solution species. Stability of the semiconductor electrodes under irradiation is thus of major concern in photoelectrochemical cells. However, stability can be attained by suitable choice of the solution redox couple or solvent and by modification of the electrode surface. An important advantage of the liquid junction cells, compared to the solid-state devices, is that the junction is produced very easily by immersing the semiconductor in solution. Moreover, light is absorbed right at the interface, so that the photogenerated carriers must move only a short distance before they react. In the Si(*p*-*n*) cell the light must pass through the layer of *p*-type material and most of the photogenerated carriers must diffuse to the junction where separation occurs. Under such circumstances expensive single crystal material is needed, otherwise recombination of the diffusing species at grain boundaries occurs before their separation, which leads to loss of efficiency. This is much less of a problem at the semiconductor-liquid interface, and polycrystalline materials (produced by vapor deposition, chemical surface treatment, or simply by pressing powdered materials into pellets) have been used successfully. Several reviews that describe the phenomena at such interfaces in more detail and discuss a number of such systems are available (*4*-*7*).

Photoelectrochemical Cells

Several different types of photoelectrochemical cells can be devised (*4*). In the liquid junction photovoltaic (or regenerative) cell the aim is the production of an electrical current flow without net changes occurring in either the electrolyte solution or the electrode materials. These cells, which are the photoelectrochemical equivalent of solid-state solar cells, utilize a single redox couple in the solution. For example, if in the cell of Fig. 2B only the redox couple D/D^+ was present, the photodriven oxidation ($D + h^+ \rightarrow D^+$) would occur at the *n*-type semiconductor electrode while the reverse reaction would occur at the metal electrode ($D^+ + e \rightarrow D$). A number of cells of this type with different semiconductor materials, redox couples, and solvents have been described. The choice of the redox couple is important, because it is a factor in fixing the operating voltage of the cell and often serves to stabilize the semiconductor from photodecomposition. For example, a cell with an *n*-CdS electrode will not operate for very long in a solution lacking a suitable redox couple, because during irradiation the photogenerated holes at the surface cause decomposition of the CdS ($CdS + 2h^+ \rightarrow Cd^{2+} + S$) rather than promoting water oxidation, and the semiconductor surface becomes covered with sulfur. In the presence of a high concentration of sulfide or selenide in the solution, however, preferential oxidation of these species occurs, and the CdS no longer decomposes (*8*). The photovoltaic cells that show the highest solar efficiencies are those using single crystal or epitaxial *n*-GaAs in an alkaline selenide electrolyte; solar power conversion efficiencies of 12 to 14 percent have been reported in these cells (*9*, *10*).

Perhaps more interesting from the viewpoint of the storage of solar energy are cells in which there is a net chemical reaction. In photoelectrosynthetic cells the overall reaction (for example, see Eq. 5) is driven in an uphill direction (that is, $\Delta G^0 > 0$ for the reaction) by the light and a portion of the solar energy is



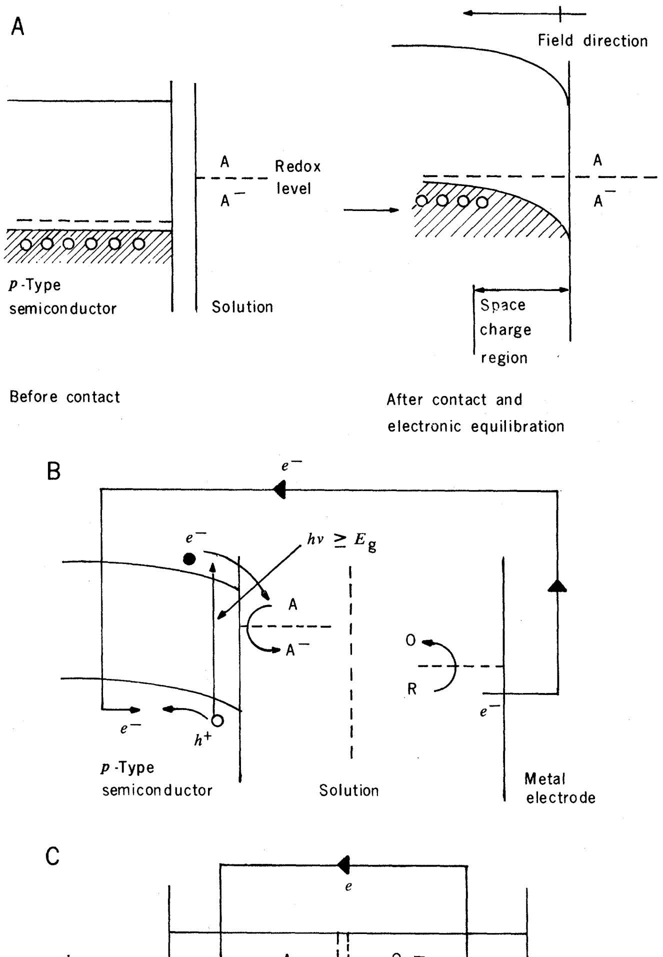


Fig. 2 (left). *n*-Type semiconductor photoelectrochemical cell. (A) Formation of space charge on immersion in solution with redox couple D/D^+. (B) Electron flow under irradiation with solution containing species D and O. (C) Cell configuration. Fig. 3 (right). *p*-Type semiconductor photoelectrochemical cell. (A) Formation of space charge on immersion in solution with redox couple A/A^-. (B) Electron flow under irradiation with solution containing species A and R. (C) Cell configuration.

stored as chemical energy in the products (R and D^+). For practical, long-term storage of fuels, the starting materials should be inexpensive, readily available materials (such as H_2O, CO, CO_2, or N_2). In an alternative arrangement the products can be used nearby, for example, in a storage battery or fuel cell arrangement where the chemical energy of the products is converted to electricity at the same time as O and D are regenerated. Photoelectrosynthetic cells have been reported, for example with *n*-$SrTiO_3$ or *n*-TiO_2 for the decomposition of water to hydrogen and oxygen (*11-13*) or with *p*-GaP for reduction of CO_2 to formaldehyde and methanol (*14*). In most cases an external electrical bias had to be provided (so that the processes were "photoassisted electrolyses" rather than purely light-driven reactions) and the solar power efficiencies were below 1 percent. Such cells could also be used for carrying out other reactions that produce chemically useful products. For example, the photooxidation of chloride has been demonstrated on *n*-TiO_2 (although again with a rather low efficiency) (*15, 16*). Thus chlorine, which is currently produced throughout the world in large amounts with the expenditure of electrical energy, could be photosynthesized by the reaction

$$2H^+ + {}^1\!/_2O_2 + 2Cl^- \rightarrow H_2O + Cl_2 \quad (7)$$

In photocatalytic cells the light is used to drive a reaction in a downhill direction (that is, $\Delta G^0 < 0$). In this case the radiant energy is not stored as chemical energy but is instead used to overcome the energy of activation of the process. Such a cell could be of interest for the decomposition of waste materials. For example, the oxidation of cyanide ion by the reaction

$$CN^- + {}^1\!/_2O_2 \rightarrow OCN^- \quad (8)$$

is spontaneous thermodynamically but is kinetically very slow. However, in a photocatalytic photoelectrochemical cell CN^- can be photooxidized at an *n*-TiO_2 electrode with O_2 reduced at a suitable cathode, so that the net reaction in Eq. 8 is accomplished (*15*). The decomposition reactions for many organic substances to smaller molecules are also spontaneous. For example, although acetic acid is usually considered to be a very stable substance, the liquid (ℓ) to gas (g) reaction

$$CH_3CO_2H(\ell) \rightarrow {}^1\!/_2C_2H_6(g) + CO_2(g) + {}^1\!/_2H_2(g) \quad (9)$$

is downhill ($\Delta G^0 = -18.4$ kJ/mole). This decomposition reaction (referred to as the Photo-Kolbe reaction by analogy to the well-known nonphotoactivated electrochemical decomposition of carboxylic acids) has also been carried out in a photoelectrochemical cell with an *n*-TiO_2 photoanode (*17, 18*).

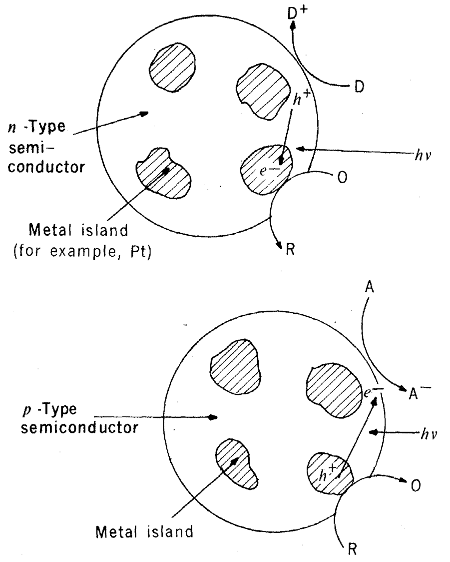


Fig. 4. Representation of semiconductor particulate systems for heterogeneous photocatalysis or photosynthesis (equivalent to the cells in Figs. 2 and 3).

Heterogeneous Photosynthesis and Photocatalysis

The concepts that emerge from studies of these types of photoelectrochemical cells with semiconductor electrodes can be applied to the design of systems in which semiconductor particles or powders are used for similar purposes. For example, we have used powders of TiO_2 with platinum dispersed on the surface for a number of studies. Each particle can be pictured as a "short-circuited" photoelectrochemical cell, where the semiconductor electrode and metal counter electrode have been brought into contact (Fig. 4). Irradiation of such particulate systems still involves the e^-h^+ pair formation and surface oxidation and reduction reactions found in the cells but without external current flow. Although powders are obviously much simpler to use, the advantage of the large separation between the oxidation and reduction sites found in the electrochemical cells is missing. However, the distance between such sites on particles is still probably large compared to those found with photochemical redox reactions in solutions, where the products of the charge transfer reaction are in close proximity within the same solvent cage.

Although the particles have been depicted in Fig. 4 as semiconductor and metal systems, in fact the untreated powders alone can often serve as photocatalytic materials. For example, the reaction of Eq. 8 can be carried out on bare TiO_2 (anatase) powders (*19*). What is required is that the reaction (in this case the reduction of oxygen) occur readily at the unilluminated TiO_2 surface. The behavior of electrodes in the photoelectrochemical cells can serve as a useful guide to the design of the catalyst particles. The rate of a reaction occurring at an electrode is measured by the current flowing through that electrode (since current flow is equivalent to charge transferred across the interface or amount of product formed per unit of time). The energy required to carry out this electrode reaction is represented by the electrode potential needed to produce this current flow. The behavior of an electrochemical cell is thus characterized by current-potential (*i-V*) curves such as those shown in Fig. 5A. These are typical of the curves found with cells of the type in Fig. 2. The oxidation of D occurs more easily on the illuminated semiconductor (Fig. 5, curve 1) than on the platinized electrode (curve 2) because the light energy promotes the electron transfer so that it takes place at less positive potentials than those corresponding to its reversible oxidation. The reduction of oxygen can occur at either the semiconductor (curve 3) or the platinum (curve 4). On the particles at steady state the net rate of the oxidation of D and reduction of oxygen must be the same. In terms of the *i-V* curves, this occurs when the anodic current has the same magnitude as the cathodic one. For the case illustrated in Fig. 5, one would predict that the platinized semiconductor would show a larger reaction rate (line a) as compared to the bare semiconductor (line b) because of the greater ease of reduction of oxygen on platinum. This application of *i-V* curves to the design of photocatalyst particles is analogous to treatments of corrosion in terms of mixed potentials and electrode kinetics (*20, 21*). In those cases the curves are usually presented in the form of log $|i|$ plotted against *V* and the intersection of the anodic and cathodic lines determines the rate of the process; this method of presentation for photoprocesses at particles is shown in Fig. 5B.

A number of heterogeneous photosynthetic and photocatalytic processes involving semiconductor particulates have been described (*4, 22, 23*); a representative sampling is shown in Table 1. Some of the same reactions that have been carried out in photoelectrochemical cells, such as the oxidation of CN^-, SO_3^{2-}, and $CH_3CO_2^-$, can also be accomplished at semiconductor powders suspended in solution. The products of the reactions may be different, however. Let us consider the oxidation of acetic acid. By application of spin trapping techniques with observation of the intermediates by electron spin resonance spectroscopy, we have demonstrated that methyl radicals ($CH_3\cdot$) are intermediates in the photooxidation at TiO_2 (*24*). Thus the elementary step in the oxidation of acetate is probably

$$CH_3CO_2^- + h^+ \rightarrow CH_3\cdot + CO_2 \quad (10)$$

where h^+ is a photogenerated hole at the semiconductor surface (or an adsorbed hydroxyl radical). In the divided photoelectrochemical cell the methyl radicals dimerize to form ethane (*17, 18*). At the platinized TiO_2 powders, however, reduction of protons to hydrogen atoms ($H\cdot$) adsorbed on the platinum sites can occur. Although some formation of ethane is observed, methane is the major product at the powders, probably because at reasonable light intensities the reaction of $CH_3\cdot$ with $H\cdot$ is more probable than coupling (*25*). The decarboxylation of a number of other acids to form the alkane at irradiated platinized TiO_2 has also been reported. The photogenerated radical intermediates in these processes have also been shown to be useful in the initiation of polymerization reactions (*26*). The advantage in this method of initiation is that the initiator radical, and the subsequent endgroup of the polymer, can be selected without regard to the light-absorption properties of the initiator.

When the solution contains ions of metals that are deposited at potentials less negative than those required for proton reduction, these ions may play the role of species, O, and be preferentially reduced at the semiconductor. This method has been applied to the deposition of platinum, copper, and other metals on TiO_2 powders, and may be useful in the preparation of catalysts (*27*). Indeed, the platinized TiO_2 particles used in the decarboxylation reactions were prepared by just this process. This technique has advantages over more conventional chemical methods of catalyst preparation in that the low temperatures used and the control over the extent of platinum deposition by the light flux allow the production of very small clusters of platinum on the semiconductor surface. The light-induced deposition of metals is clearly related to photographic processes (*28*). Fundamental studies of the behavior of semiconductor electrodes and powders can provide insight into the physical and chemical processes occurring during image formation and may also be useful in the fabrication of new types of electrochromic devices for use in displays. Photoprocesses at TiO_2 and ZnO may also be implicated in the chalking of paints with these pigments (*29*); chalking occurs in exterior paints when the organic polymer binder is degraded and the pigment is exposed on the surface.

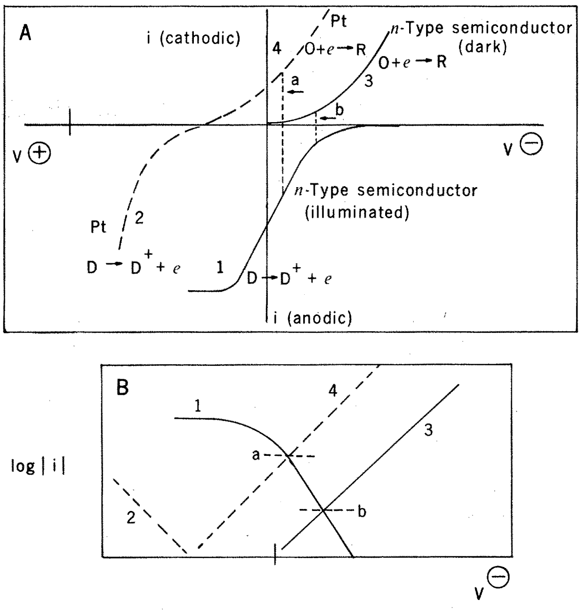


Fig. 5. The application of current-potential curves in the design of photoelectrochemical systems. (A) Representative curves for the system in Fig. 2. Solid lines indicate behavior at *n*-type semiconductor (curves 1 and 3); broken lines, at Pt metal (curves 2 and 4); *a*, operating point for semiconductor/Pt system; *b*, operating point for bare semiconductor system. (B) Curves showing log current plotted against potential for the system in (A).

Perhaps the area of application of greatest potential utility, but also the one with the most serious difficulties, is that of photoelectrosynthesis of useful chemicals from inexpensive and abundant materials (for example, H_2 from H_2O, CH_3OH from CO_2, and NH_3 from N_2). Several experiments (see Table 1) demonstrate the feasibility of such processes but so far both the quantum efficiency (molecules of product produced per photon absorbed) and solar efficiency (molecules of product produced per incident solar photon) have been rather low (usually less than 1 to 2 percent). These low efficiencies can be ascribed to problems caused by recombination of products and intermediates as well as the use of materials whose band gap is too large to utilize effectively the solar spectrum. Recent considerations of the photodecomposition of water by semiconductor systems or by other means with sunlight suggest that when the needed energy and driving forces are considered, a single light-absorbing system necessitates the use of a semiconductor with a rather large band gap (2.5 to 3.0 eV) (*2, 4*). The efficient utilization of solar energy for water-splitting may thus require the strategy of green plants, that is, the use of two photosystems with the absorption of the two photons of lower energy per electron transferred.

We have discussed the possibility that such photoprocesses on semiconductors, presumably taking place on naturally occurring powders, played a role in

Table 1. Representative heterogeneous photocatalytic and photosynthetic processes at semiconductor powders.

Reaction	Powder	Comments	Reference
	Liquid phase		
$O_2 \rightarrow H_2O_2$	ZnO, others	Oxidation of organic additives	(*22*)
$RCO_2H \rightarrow RH + CO_2$	Pt/TiO_2	$R = CH_3, C_2H_5, \ldots$	(*25*)
$M^{+n} \rightarrow M$	TiO_2,WO_3	M = Pt, Pd, Cu, . . .	(*27, 33*)
$CN^- \rightarrow NCO^-$	TiO_2, ZnO, CdS	Reduction of O_2	(*19*)
$CO_2 \rightarrow CH_3OH,HCHO$	TiO_2, CdS. . . SiC, GaP		(*34*)
$H_2O \rightarrow H_2 + O_2$	Pt/TiO_2, $Pt/SrTiO_3$		(*11, 35*)
$O_2 \rightarrow O_2^-\cdot$	CdS		(*36*)
	Gas phase		
$CO \rightarrow CO_2$	ZnO		(*22, 23*)
$N_2 \rightarrow NH_3$	TiO_2(Fe-doped)		(*37*)
RH → ketones	TiO_2		(*23, 38*)
Quinoline → radical cation	TiO_2		(*39*)

early chemical evolution on earth (*30*). Irradiation of mixtures of NH_3, methane, and water in the presence of platinized TiO_2 with either a xenon lamp or sunlight was shown to produce amino acids. This experiment is thus similar to those demonstrating the production of amino acids in electric discharges or by ultraviolet light (*31, 32*), but demonstrates that light within the solar spectrum is capable of promoting such a reaction. In the absence of the semiconductor such processes would not be possible, because none of the components of the mixture absorb radiation in the visible and near ultraviolet region. This type of process for the formation of amino acids from components of the primordial atmosphere is attractive, because it provides a means for their continuous production over long periods of time, thus providing nutrients for early heterotrophic organisms with energy inputs not very different from those on the earth now. Although platinized TiO_2 is an unlikely candidate for such a process under natural conditions, many other semiconductor powders, such as WO_3, Fe_2O_3, and ZnO that have been used for photocatalytic processes, might also be capable of such an inorganic photosynthesis. The role of similar processes as a nonbiological source of oxygen in the early atmosphere might also be considered.

Conclusions

The basic principles of photoelectrochemical cells and the photoprocesses occurring on semiconductor materials have been established and studies describing new materials and reaction schemes are appearing with increasing frequency. Although more efficient systems utilizing inexpensive and readily available semiconductors are still needed, the field of photoelectrochemistry has opened new areas in electrochemical research and has provided new insight into the interactions of light, electricity, and chemical reactions in a number of different processes.

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