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PHOTOELECTROSYNTHESIS AT
SEMICONDUCTOR ELECTRODES

MASTER

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I. Introduction

The field of photoelectrochemistry is currently enjoying a period of exciting new developments, rapid progress in both theory and applications, and attraction for scientists in a broad range of disciplines. This is because photoelectrochemical systems have shown an excellent capability to perform the three functions required for the photochemical conversion and storage of solar energy; namely: (1) efficient absorption of sunlight to produce electrons and positive holes; (2) efficient separation and stabilization of the photogenerated positive and negative charge carriers; and (3) efficient subsequent redox chemistry to yield oxidized and reduced chemical species.

The other approaches to the problem of chemical conversion of solar energy, all of which are discussed at this conference, have many common elements with each other and with photoelectrochemistry; conferences such as the present one serve the very important function of inducing communication and interaction between the scientists involved in these various approaches. This is most critical, since the three requirements listed above are so difficult and demanding in a practical solar energy conversion system, where system lifetime must be in the order of decades, that the optimum scheme must incorporate the best features of each approach.

This necessity is apparent, for example, in the case of the solar-driven water splitting reaction by photoelectrochemical and photochemical systems. These two apparently different approaches, one involving semiconductor materials and the other photochemical redox species, are converging in one particular scheme to a common configuration. This configuration involves small particulate systems; in photoelectrochemistry these are called photochemical diodes (1,2) and in photochemistry these are called micro-heterogeneous redox systems (3). In the latest version of these particulate systems, as described by Professor Grätzel at this and other recent conferences (3), the particles consist of semiconductor powders (TiO_2) that have molecular sensitizers ($\text{Ru}(\text{bpy})_3$) and catalytic species (Pt and RuO_2) associated with the surface. The molecular sensitizer permits efficient absorption of visible light, the semiconductor permits efficient charge separation and stabilization, while the Pt and RuO_2 catalysts permit efficient water reduction and oxidation, respectively, to yield H_2 and O_2 (4). Thus, the best qualities of each system (dye, semiconductor, catalyst) are combined

to yield a working system for photochemical water splitting with sunlight. Future interactions between photoelectrochemistry and photochemistry promise to produce equally interesting and significant advances.

In this paper, I will first review the general principles of photoelectrochemistry and photoelectrosynthesis, and I will then discuss a half-dozen new developments in photoelectrosynthesis.

II. Brief Review of Photoelectrochemical Energy Conversion

Photoelectrochemical systems are defined as those wherein a photoactive semiconductor material is in contact with a liquid (or solid) electrolyte, and a junction is formed between the semiconductor and the electrolyte such that the illumination of the semiconductor with light equal to or greater than the semiconductor band gap produces electrons and holes that spatially separate, because of the junction potential, and subsequently drive chemical reduction and oxidation reactions in the system. Photoelectrochemical systems are distinguished from the photogalvanic systems described in detail in this conference by Professor Archer, in that in the latter the light is absorbed by molecular pigments in solution.

A general classification scheme for the various types of photoelectrochemical cells is shown in Figure 1. One can first divide the cells into (a) those wherein the free energy change in the electrolyte is zero (these are called electrochemical photovoltaic cells); and (b) those wherein the free energy change in the electrolyte is non-zero (these are called photoelectrosynthetic cells).

In the photoelectrosynthetic cell, two different redox couples are present and two different redox reactions occur at the electrodes upon illumination, producing a net chemical change. If the free energy change of the net electrolyte reaction is positive, optical energy is converted into chemical energy (an endoergic process). However, if the net electrolyte reaction has a negative free energy change, optical energy provides the activation energy for the reaction (an exoergic process). In previous discussions (2,5,6,7) the latter situation was termed photocatalytic because the light was acting to speed-up a thermodynamically downhill reaction. However, it is also possible to have catalytic effects in the case of thermodynamically uphill reactions that are driven by light. Hence, a more

appropriate label for the two types of photoelectrosynthetic reactions might be endoergic photoelectrosynthesis and exoergic photoelectrosynthesis.

The potential advantages of photoelectrochemical energy conversion compared to solid state photovoltaic systems are listed in Table I. Electrochemical photovoltaic cells are discussed at this conference by Dr. Memming. The present paper will only be concerned with photoelectrosynthetic cells. Energy level diagrams for the two types of photoelectrosynthetic cells are presented in Figure 2 (5,6,7).

For efficient photoelectrosynthesis, three parameters must be simultaneously optimized: (a) the semiconductor band gap must be as small as possible to maximize the absorption of sunlight but large enough to provide the chemical potential for the desired chemical reaction; (b) the flat-band potential (electrode potential at which the semiconductor bands exhibit no band bending) must be matched to the redox chemistry in the electrolyte so that the desired chemical reaction can proceed at a sufficiently fast rate with minimum or no external bias voltage; and (c) the semiconductor electrode system must be stable for very long periods of time. It has not yet been possible to find a photoelectrosynthetic system that exhibits all three characteristics together with high conversion efficiency. Many reviews are available (8-13) that describe these problems in detail.

III. New Developments in Photoelectrosynthesis

A. Energetics of Semiconductor-Electrolyte Interfaces: Band-Edge Unpinning

In the conventional model of semiconductor-electrolyte junctions (8-13) it is assumed that changes in applied potential appear across the semiconductor space charge layer and that the drop across the Helmholtz layer is constant. This means that the positions of the semiconductor band edges are fixed or pinned with respect to the redox energy levels in the electrolyte, and that they do not change with electrode potential. This leads further to the restriction that only redox couples lying within the semiconductor band gap can undergo photoinduced redox chemistry. In the absence of hot carrier injection (to be discussed in the next section), photogenerated electrons and holes are injected into the electrolyte at the bottom of the conduction and valence bands at the interface. Hence, redox

couples lying outside the band gap are inaccessible to electron reduction or hole oxidation (see Figure 3).

However, recent experiments with Si, GaAs, and MX_2 ($M = \text{Mo}, \text{W}, X = \text{S}, \text{Se}, \text{Te}$) indicate that the band edges can become unpinned, and that applied potentials can shift the semiconductor band positions with respect to the electrolyte redox levels. The effect here is to be able to oxidize or reduce redox couples that lie outside the band gap as determined from values of the flat-band potential obtained in the dark. Several explanations for the unpinning of the bands have been proposed.

One explanation (14) is based on the concept of Fermi level pinning as commonly observed in solid state Schottky barriers (15). In this model, it is believed that a high density of surface states pin the Fermi level and produce band bending that is independent of the redox potential of the electrolyte. Photoelectrochemical experiments with MoSe_2 , GaAs and Si (16,17) show that: (a) a number of A^+/A systems with widely different redox potentials produce the same photovoltage for a given semiconductor; (b) certain A^+/A systems produce photovoltages even when the redox potentials are outside the band gap; and (c) photoeffects can be found for redox couples with redox potentials that span a range greater than the semiconductor band gap. If the Fermi level is pinned by surface states, then the system is equivalent to a solid state Schottky barrier in series contact with electrolyte, such that the band edges move with applied potential while maintaining a constant band bending. This situation is shown in the energy level diagram of Figure 4. Further research is required to establish the generality and significance of Fermi level pinning effects in photoelectrosynthesis.

Another explanation for band-edge shifting or unpinning with applied potential applies to small band gap semiconductors where inversion can occur (18,19). When the band bending in the semiconductor is sufficiently large such that the Fermi level at the surface lies closer to the minority carrier band than to the majority carrier band, then the surface becomes inverted and a large charge density develops in the semiconductor space charge layer (see Figure 5). Under conditions of inversion the charge density and capacitance of the semiconductor space charge layer becomes comparable to or larger than the charge density and capacitance of the Helmholtz layer, (see Figure 6), such that additional potential changes applied to the electrode appear across the Helmholtz layer. This situation results in band-edge unpinning.

The presence of inversion, and subsequent band-edge unpinning, can be followed through capacitance data. In the ideal case (20), the capacitance decreases in the depletion region (following the Mott-Schottky relationship) and reaches a minimum value at the onset of the inversion region. As the inversion region develops, the space-charge density increases rapidly. The effect of this increased charge density on the measured capacitance depends upon the frequency of the applied ac signal. At high frequency (>100 Hz) the electron concentration cannot follow the ac signal, and the measured capacitance is flat and minimized in the inversion region. However, at low frequency (<100 Hz) the electrons in the space-charge layer can follow the ac signal and the capacitance increases rapidly with the increased degree of inversion. The effect of illumination in these experiments is to increase the measured capacitance in the inversion region at the high frequencies such that the low frequency behavior is produced (20). This characteristic dependence of capacitance on potential, frequency, and light intensity is shown in Figure 7 for p-Si with a thin (600 Å) oxide layer. The oxide layer thickness is another parameter governing the detailed characteristic behavior of the capacitance in the inversion region (20).

Experiments (18,19,21) with p-Si electrodes in acetonitrile and methanol show that the capacitance as a function of potential, frequency, light dependence and oxide thickness show nearly the ideal behavior described above for the inversion region of p-Si. Hence, the reduction of redox couples (such as anthraquinone, nitronaphthalene, dimethoxynitrobenzene, and dichloronitrobenzene) that lie above (more negative than) the conduction band edge of p-Si can be explained by band-edge unpinning that arises from the development of an inversion layer in the electrode; these supra-band-edge reductions occur at potentials where the capacitance data exhibited the characteristics of the inversion region (18,19).

B. Hot Carrier Injection at Illuminated Semiconductor-Electrolyte Junctions

As discussed in Section III-B, it has generally been assumed in photoelectrochemistry that the energy of injected photogenerated carriers is given by the position of the minority carrier band edge at the semiconductor-electrolyte interface. That is, carriers are accelerated to the surface by the electric field in the semiconductor space charge layer, but they lose

energy (as heat) in the process via carrier-phonon collisions. As a result, the carriers are in thermal equilibrium with the lattice before injection.

In a modification of this model (22,23), it has recently been proposed that photogenerated minority carriers which have not undergone full intraband relaxation may also be injected into the electrolyte; this process is called hot carrier injection (see Figure 3). This process can occur if the thermalization time (T_{Th}) of the photogenerated carriers in the semiconductor space charge layer is greater than both the charge transfer or tunneling time of the carriers into the electrolyte and the effective relaxation time of the injected carriers in the electrolyte. These various characteristic times are shown in Figure 8 for electron injection from a p-type semiconductor.

The calculations for the various characteristic times have been estimated using classical and quantum mechanical models (6,22,23). In one particular model (22), the aqueous electrolyte is treated as a large gap semiconductor and photoexcited carriers find themselves in the potential well created by the position-dependent potential in the semiconductor-electrolyte barrier. This well has characteristic quantized levels and carriers can be injected from these quantized levels into the electrolyte. Photogenerated electrons may either cascade down the quantized levels, i.e., thermalize, or they may tunnel through the surface barrier into the electrolyte.

The basic quantum mechanical problem to be solved is to first find the eigenstates for the potential well in the semiconductor. From the nature of these solutions the properties of the system are deduced in terms of the following characteristic times: T_{Th} , the time for thermal relaxation of an electron in an excited state in the depletion layer; T_t , the time required for the carrier to be transferred to the ion in the electrolyte; and T_r , the time required for the ionic energy level to relax by reorientation of solvent dipolar species surrounding the ion such that reverse tunneling from the electrolyte to the semiconductor is prevented. These calculations are described in detail in reference 22; the results are comparable to those based on classical and simpler quantum mechanical models (6).

From these analyses and calculations several general criteria for obtaining hot carrier injection at semiconductor-electrolyte junctions are evident. The overall criterion is that both the tunneling time of the photogenerated minority carriers and the effective relaxation time of the

electrolyte must be faster than the thermalization time of these carriers in the semiconductor.

Strong electronic-vibrational interaction in the electrolyte renders the tunneling process from the semiconductor irreversible, obviating oscillations which increase residence time in the semiconductor and thus intraband thermalization. This irreversibility has its basic origin in the electronic particle tunneling from the semiconductor where the electron-phonon interaction is weak, to the electrolyte, where the electron-phonon interaction is strong.

Hot carrier injection is favored in semiconductor electrodes which have a low effective mass for the minority carrier. This is because a low effective mass will produce more widely-spaced quantized levels in the depletion layer which then results in long intraband (now interlevel) thermalization times. Low minority carrier effective mass also means that the part of the photon energy which exceeds the band gap will preferentially go to the minority carrier; this will produce hot carriers in the depletion region by virtue of absorption of photons with energy greater than the band gap. In this case, hot carrier injection is more favored in direct band gap semiconductors.

Heavy doping will also favor hot carrier injection because the depletion layer thickness will be reduced. This effect leads to enhanced quantization in the depletion layer, and hence, longer thermalization times.

The occurrence of hot carrier injection in photoelectrochemical reactions would be very significant for the following reasons: (1) the nature of the permitted photoinduced reactions at semiconductor electrodes could be more readily controlled by the electrode potential; (2) the photogenerated carriers would not be in thermal equilibrium in their respective bands so that quasi-thermodynamic arguments, such as the use of the quasi-Fermi level to describe the energetics of photoelectrochemical reactions would not be valid; (3) the influence of surface states would be restricted to the class of states originating from the chemical interaction of the electrolyte with the semiconductor surface; and (4) the maximum theoretical conversion efficiency for photoelectrochemical energy conversion may be much greater compared with the case of thermalized injection; initial estimates (24) of the theoretical thermodynamic limit indicate that the efficiency of the hot carrier pathway may be twice that of the thermalized pathway.

The existence of hot carrier injection has not yet been experimentally verified. Experiments designed to probe for hot carrier injection by studying supra-band-edge redox reaction (18,19) were inconclusive because of the band-edge unpinning effects discussed in Section III-A. Additional research must be done to unequivocally establish the significance of hot carrier injection in photoelectrochemical systems.

C. Derivatized Semiconductor Electrodes

The photogenerated holes and electrons in semiconductor electrodes are generally characterized by strong oxidizing and reducing potentials, respectively. Instead of being injected into the electrolyte to drive redox reactions, these holes and electrons may oxidize or reduce the semiconductor itself, and cause decomposition. This possibility is a serious problem for practical photoelectrochemical devices, since photodecomposition of the electrode leads to inoperability or to short electrode lifetimes.

A simple model of electrode stability has been presented (25,26) wherein the redox potential of the oxidative and reductive decomposition reactions are calculated and put on an energy level diagram like Figure 2. The relative positions of the decomposition reactions are compared with those of the semiconductor valence and conduction band edges. Absolute thermodynamic stability of the electrode is assured if the redox potential of the oxidative decomposition reaction of the semiconductor lies below (has a more positive value than) the valence band edge, and if the redox potential of the reductive decomposition reaction lies above (has a more negative value) the conduction band edge. This situation does not exist in any of the semiconductors studied to date. More typically, one or both of the redox potentials of the semiconductor oxidative and reductive decomposition reactions lie within the band gap, and hence become thermodynamically possible. Electrode stability then depends upon the competition between thermodynamically possible redox reactions in the electrolyte. This competition is governed by the relative kinetics of the possible types of reactions.

In cases where the redox potentials of the electrode decomposition reactions are more thermodynamically favored than the electrolyte redox reactions (oxidative decomposition potential more negative, reductive decomposition potential more positive, than the corresponding electrolyte redox reactions), the products of the electrolyte redox reactions have

sufficient potential to drive the electrode decomposition reactions. Hence this situation usually results in electrode instability, assuming that the electrode decomposition reaction is not kinetically inhibited.

It is frequently the case in photoelectrochemistry that the more thermodynamically favored oxidation reactions also become kinetically favored, so that these reactions predominate. This effect has been used to stabilize n-type semiconductor electrodes by establishing a redox couple in the electrolyte with a redox potential more negative than the oxidative decomposition potential such that this electrolyte redox reaction occurs preferentially compared to the decomposition reaction, and scavenges the photogenerated minority carriers. However, this particular stabilization technique can only be used for electrochemical photovoltaic cells since in photoelectrosynthesis the permitted electrode reactions are dictated by the desired overall chemical reaction of the system.

One method of electrode stabilization involves chemical derivatization of the semiconductor surface. It has been shown (27) that covalent attachment of redox species to semiconductor surfaces can effect the kinetics of charge transfer across semiconductor-electrolyte junctions such that less thermodynamically favored reactions predominate over thermodynamically favored reactions. For example (27,28), illumination of n-type Si modified with a ferrocene derivative will not result in the thermodynamically favored oxidation of Si to SiO₂, but rather will result in the oxidation of Fe(CN)₆⁴⁻ to Fe(CN)₆³⁻ in the electrolyte. The chemically attached ferrocene species act as a hole mediator for n-Si, and channels the photogenerated hole to the Fe(CN)₆⁴⁻/Fe(CN)₆³⁻ redox reaction rather than to the Si/SiO₂ reaction (see Figure 9). This effect can be very important for stabilizing electrodes both in electrochemical photovoltaic cells and photoelectrosynthetic cells. For example, in Figure 10, derivatization of the semiconductor AB with R-D/D⁺ would result in photogenerated charge being channeled through the surface attached D/D⁺ couple to the H₂O₂ reaction, rather than to the oxidation of AB to B and A⁺; the stepwise and net reactions for this sequence are indicated in the figure. Such charge mediation effects are analogous to the function of the Mn-complex in Photosystem II in photosynthesis; in that case, photogenerated holes are also channeled to the H₂O oxidation reaction, rather than to the oxidation of the chlorophyll molecule itself.

In addition to enhancing the stability of semiconductor electrodes, chemical derivatization or modification of the semiconductor surface can also be used to increase the catalytic activity of the electrode surface (29). This has been demonstrated (29) for p-type Si in aqueous electrolyte. Normally it is difficult to evolve H_2 on p-type electrodes, and a large negative deviation from the flat-band potential is required before H_2 evolution is achieved. However, by binding a paraquat (PQ^{2+}) derivative to the surface, the photogenerated electron is first efficiently captured by the PQ^{2+} species attached to the surface, and the reduced PQ^+ species then reduces H^+ to H_2 . The overall effect is that H_2 is evolved at a much less negative potential than required for the electrode without surface modification; that is, the derivatized surface shows electrocatalytic activity.

D. Particulate Photoelectrochemical Systems

Because of its inherent simplicity, a photoelectrosynthetic system that consists of microscopic semiconductor particles suspended in electrolyte is an intriguing and potentially very important type of configuration. Particulate photoelectrosynthetic systems are being studied by several workers (1-4,7) and such particulates have been labeled photochemical diodes (1).

The most efficient photoelectrochemical particles or photochemical diodes have a heterogeneous structure with an n-type region in contact (through a non-blocking, ohmic-like junction) either to a metal or to a p-type region. The energetics of these heterogeneous structures result in the most efficient system for the spatial separation of photogenerated electrons and holes (1); electrons are readily removed from the metal or p-type regions, while holes are easily removed from the n-type region to drive reduction and oxidation reactions, respectively, in the electrolyte. Such heterogeneous photochemical diodes have been used to split water (1,10,30), decarboxylate organic acids via a photo-Kolbe reaction (31,32), oxidize organic compounds (33), photoreduce N_2 (34,35), and photoreduce CO_2 (36,37).

In addition to the heterogeneous structures, homogeneous semiconductor particles have also been shown to drive photoelectrosynthetic reactions (31,32,36,37). In the homogeneous case, the band bending at the liquid interface would be in the same direction everywhere, and this would result in a potential well for the majority charge carrier. This potential well would inhibit majority carrier charge transfer from the semiconductor to the

electrolyte, depending upon the width and height of the barrier. Experimental results comparing homogeneous and heterogeneous semiconductor particles (31,32,36,37) show that indeed the reaction rate on heterogeneous particles is much greater than that on homogeneous particles.

Work on single crystal SrTiO_3 (30) shows that photoinduced water splitting can occur without platinization of one surface if the water layer in contact with the illuminated surface has a very high OH^- concentration. The rate of H_2O splitting is highest if a photochemical diode is formed by attaching a platinum layer to the back of the crystal, but a finite rate of H_2O splitting can also be produced without a platinum layer. Even if the SrTiO_3 crystal is not reduced (to make it conductive), and the bands are consequently flat, a finite rate of H_2O splitting can be observed. The non-platinized, but reduced, SrTiO_3 permits electron injection either by tunneling through the barrier or by photoexcitation over the barrier. Electron and hole injection from unreduced and non-platinized SrTiO_3 would also depend upon the relative rates of bulk diffusion versus recombination. The dramatic effect of the OH^- concentration on the rate of H_2O splitting is not understood.

The advantage of homogeneous particles is their simple structure. However, heterogeneous photochemical diodes consisting of metal-semiconductor structures can also be simply made by in-situ photoreduction of metal ions onto the semiconductor particle (2,7,31,32). A simple method for producing photochemical diodes containing the n- and p-type semiconductor configuration has not yet been developed.

A particularly interesting example of a heterogeneous photochemical diode is the micro-heterogeneous redox system described by Gratzel and co-workers (3). It has been pointed out (4) that these micro-heterogeneous redox systems are dye-sensitized photochemical diodes containing an oxidation catalyst (RuO_2) and a reduction catalyst (Pt) on the surface. The dye is $(\text{Ru}(\text{bpy})_3)$, which when excited by visible light injects electrons into the conduction band of the TiO_2 semiconductor support to form an oxidized dye species that subsequently oxidizes water to O_2 in the presence of the RuO_2 catalyst. The injected electrons move through the TiO_2 conduction band and reduce water to H_2 at the Pt sites.

E. Layered Compounds and Other New Materials

A very active area of research in photoelectrosynthesis involves the study of new semiconductor electrode materials. Layered chalcogenide compounds are particularly interesting since the top of the valence band is comprised of metal d_z^2 orbitals rather than anion 4p orbitals (39). This means that an optical transition near the band gap energy involves only metal to metal transitions (the conduction band is also made of d-like metal orbitals) and does not disrupt a metal-anion bond. This type of optical transition is believed to be less susceptible to photocorrosion than the usual transitions involving anion-like orbitals in the valence band (39). An alternative explanation for the stability has been proposed (40) that is based on screening of the metal ions by the covalently bonded chalcogenide layers such that solvation of the metal ions by the electrolyte is prevented.

Results (41-45) with layered chalcogenides such as MoS_2 ($E_g = 1.8$ eV), MoSe_2 ($E_g = 1.4$ eV), MoTe_2 ($E_g = 1.0$ eV), WSe_2 ($E_g = 1.6$ eV), and WS_2 ($E_g = 2.0$ eV) show that enhanced resistance to photocorrosion is indeed observed. However, photocorrosion readily occurs at the edges of layered materials (11 to C-axis), and this presents problems for the planar face also since atomic-sized step dislocations in the surface become photocorrosion sites.

Another class of semiconductor compounds that is receiving attention is the oxides. The oxide semiconductors are generally the most stable materials for the photooxidation of water to O_2 , but their band gaps are too large. Attempts are being made (46-49) to reduce oxide band gaps by creating d-bands above the oxygen 2p band. However, one major problem with this approach is the low hole mobility expected for these systems.

F. Dye Sensitization

A great deal of work is in progress (50-54) on improving the visible response of large band gap, but relatively stable, semiconductor electrodes by dye sensitization techniques. The general mechanism for this approach is shown in Figure 11. A dye (A) with strong absorption properties in the visible is bonded to the semiconductor surface. Upon excitation to A^* , an electron is transferred to the semiconductor conduction band leaving A^+ at the surface. The electron in the semiconductor subsequently reduces H^+ to H_2 at a metal cathode, while A^+ oxidizes H_2O to O_2 to regenerate A. As seen in Figure

11, the net overall reaction is the photolysis of H_2O into H_2 and O_2 .

The problems associated with dye sensitization are: (1) the dyes are generally organic species that have relatively poor long term stability and do not survive the repeated oxidation-reduction cycles; (2) the dye layer on the electrode must be very thin to permit charge transfer from the excited dye to the electrode, but this requirement often is in conflict with the dye layer also exhibiting intense optical absorption; and (3) certain dye-semiconductor electrode combinations show very low quantum efficiencies for electron transfer to semiconductor electrodes from dye molecules ranging from 4×10^{-3} for the rose bengal- TiO_2 system (53), to 1.0 for the tris (4,7-dimethyl-1, 10-phenanthroline) ruthenium (II) system (54).

To date, no system has been found that exhibits total conversion efficiencies greater than about 1% coupled with long-term stability.

Conclusion

The photoelectrosynthetic approach to solar energy conversion is very appealing and exciting; very good progress is being made both in the basic understanding of photoelectrochemical phenomena and in applied systems. The potential advantages of photoelectrosynthesis over photovoltaics coupled to dark electrosynthesis are in higher net conversion efficiency, better engineering designs for solar reactors, and unique catalytic effects possible with modified semiconductor electrode surfaces.

The main problem in the field is the lack of semiconductor materials that exhibit high conversion efficiency and long term stability. However, one very promising approach involves the chemical modification or derivatization of the semiconductor surface to enhance photo-stability and catalytic activity. This approach is interesting in that it represents a common intersection with the current directions of photochemical approaches to solar energy conversion (3). In the latter, systems are being studied that involve semiconductor particles as catalysts to help drive the photochemical redox reactions. These semiconductors act as electron pools to facilitate the redox chemistry and catalyze the desired reactions.

It appears that the optimum photoelectrosynthetic system may involve semiconductors (to absorb the light and separate the photo-induced charge

carriers); in the form of fine particles (for optimum engineering design), but modified on the surface with chemical compounds (to enhance stability, catalytic activity, and perhaps also optical absorptivity).

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TABLE I Potential Advantages of Photoelectrochemical Cells

Electrochemical Photovoltaic Cells

Junction formation is very simple.

Efficiencies of polycrystalline thin film electrodes are comparable to those of single crystal electrodes.

In situ storage capability can be introduced into the cell.

Photoelectrosynthetic Cells

For water splitting, the theoretical conversion efficiency is significantly higher than photovoltaics followed by electrolysis.

Particulate reactor systems can be used (photochemical diodes).

Novel reactions products are possible.

Catalytic effects can be introduced on the semiconductor electrode surface.

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FIGURE CAPTION

- Figure 1 Classification of photoelectrochemical cells.
- Figure 2 Energy level diagrams for endoergic and exoergic photoelectrosynthetic cells.
- Figure 3 Two classes of photogenerated electron injection from a p-type semiconductor into liquid electrolyte. Hot electron injection occurs if the photogenerated electron is injected into the electrolyte to reduce A to A^- before it is thermalized in the space-charge layer via electron-phonon collisions. A thermalized electron, emerging at the conduction band edge (E_c), would have insufficient energy to drive a redox couple A/A^- lying above E_c .
- Figure 4 Fermi-level pinning by surface states leading to the movement, or unpinning, of the semiconductor band edges at the semiconductor-electrolyte interface.
- Figure 5 Inversion in p-type semiconductors arising from large band-bending.
- Figure 6 Calculated space-charge density of p-type Si as a function of band bending. Band-edge unpinning may occur in the inversion region because of the higher charge density that develops (Ref. 20).
- Figure 7 Ideal capacitance-voltage behavior as a function of frequency and light intensity for a semiconductor in the accumulation, depletion, and inversion regions (Ref. 20).

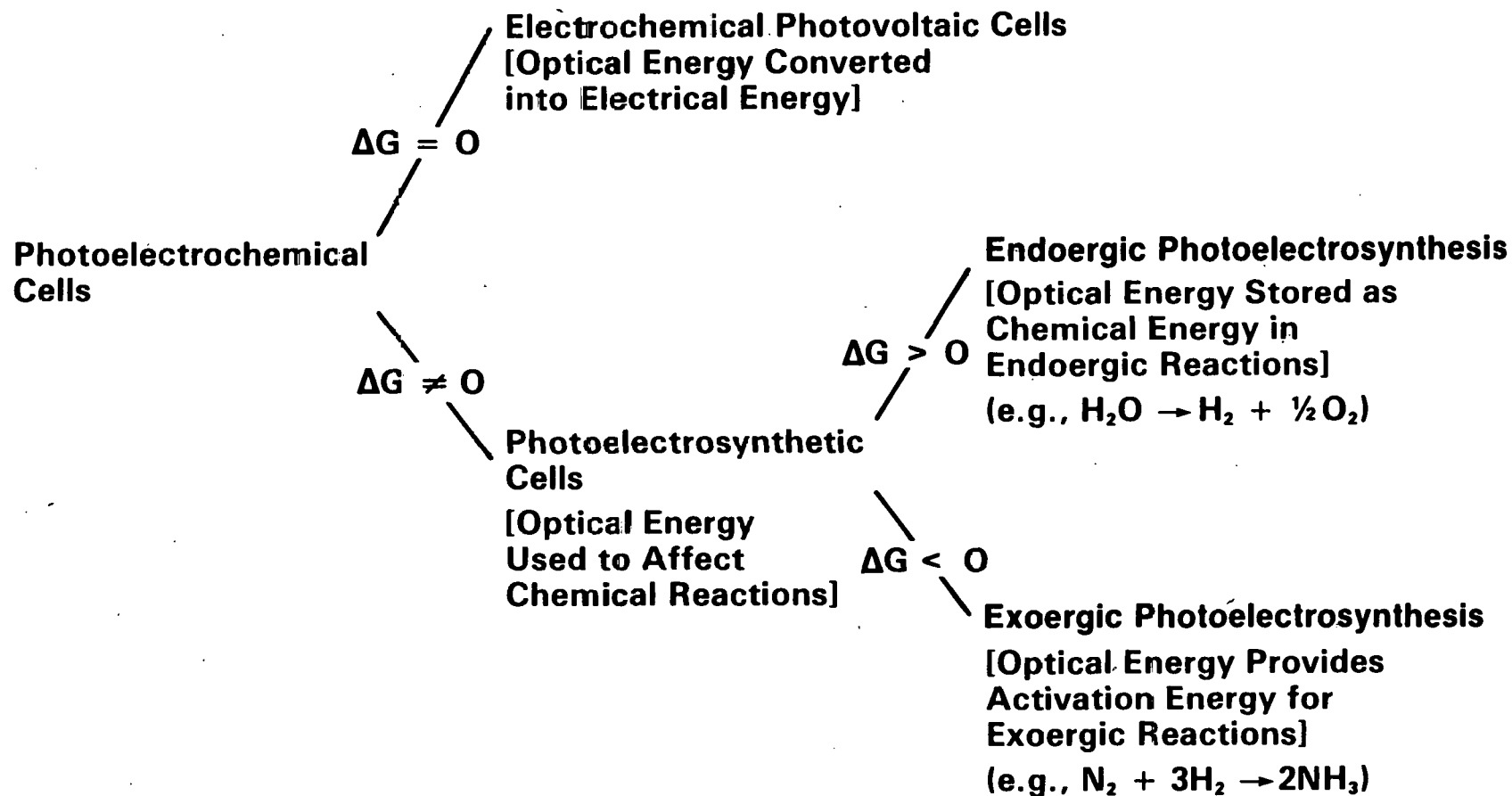
Figure 8 Hot electron injection from p-type semiconductors showing the characteristic time constants for competing de-excitation pathways. T_T is the tunnelling or charge transfer time to the electrolyte of the non-thermalized electron, T_{Th} is the electron thermalization time in the semiconductor space charge layer, T_R is the effective relaxation time in the electrolyte to prevent back electron transfer to the semiconductor, and T_{CT} is the charge transfer time of the thermalized electron.

Figure 9 n-Type silicon derivatized with ferrocene to permit oxidation of $Fe(CN)_6^{4-}$ to $Fe(CN)_6^{3-}$ in solution and prevent the oxidation of the silicon surface to SiO_2 .

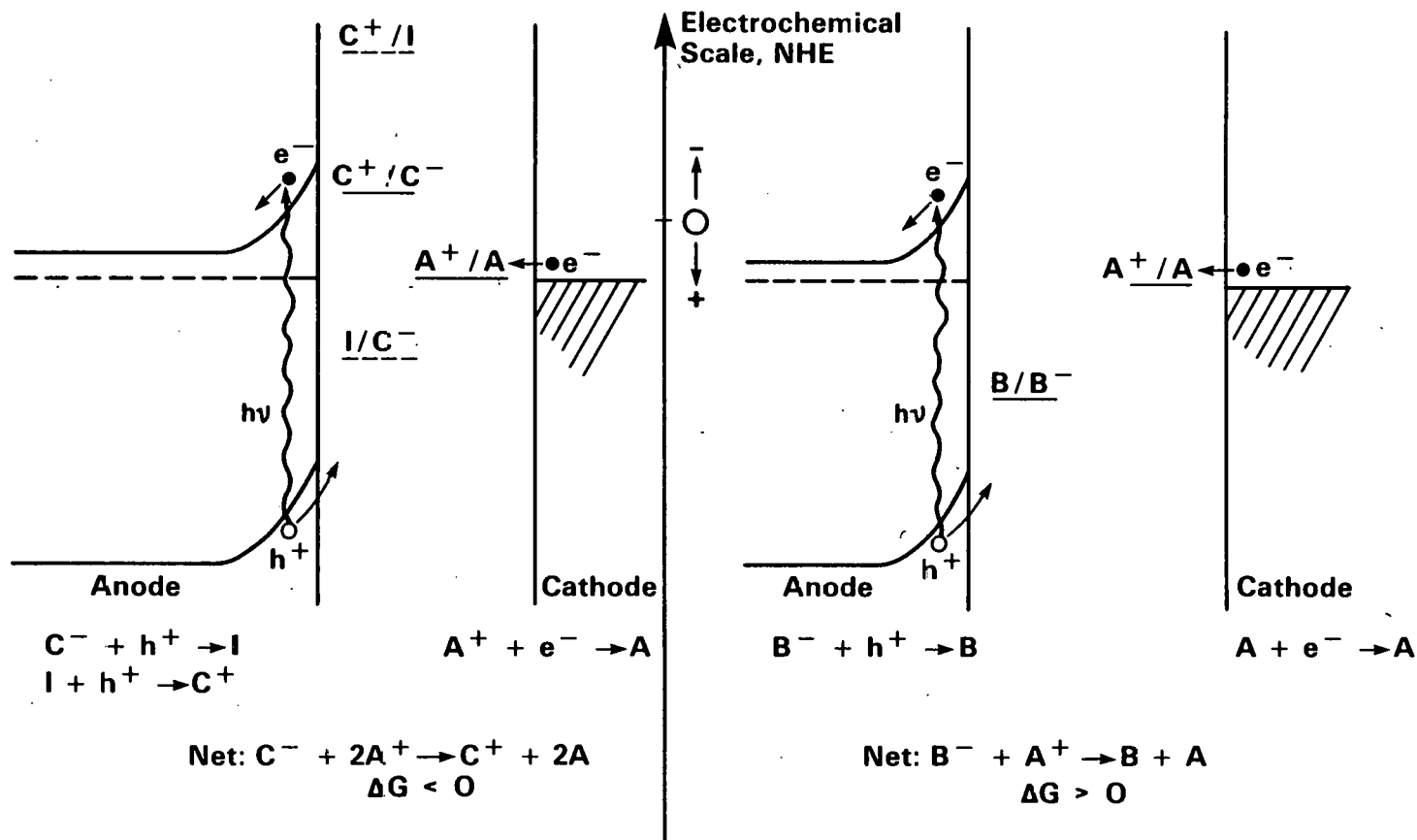
Figure 10 General scheme for the chemical modification of an n-type semiconductor surface to yield photooxidation of H_2O to O_2 rather than the self-oxidation of the semiconductor itself.

Figure 11 Energy level scheme for dye sensitization of n-type semiconductor electrodes.

Classification of Photoelectrochemical Cells



Photoelectrosynthetic Cells

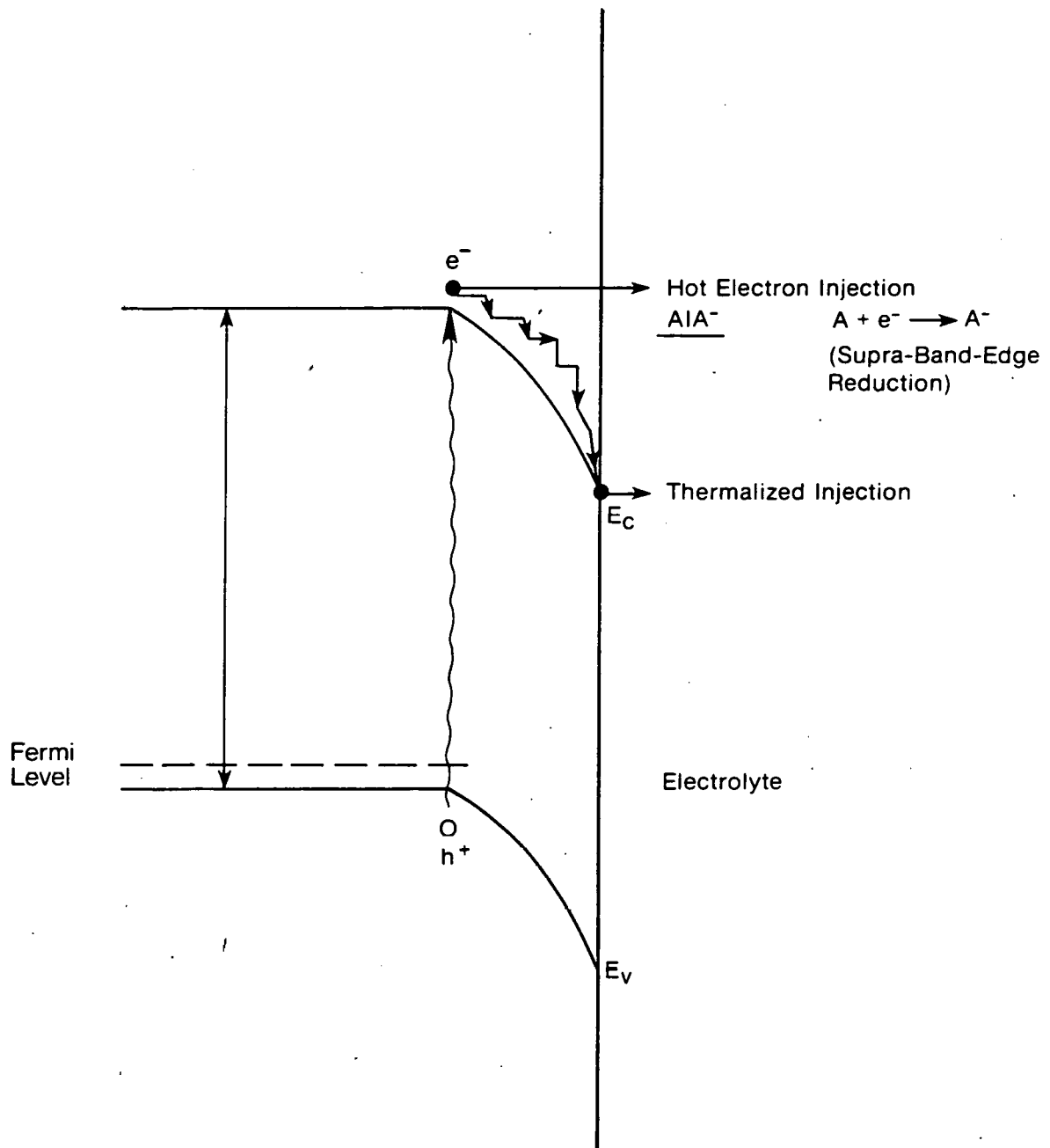


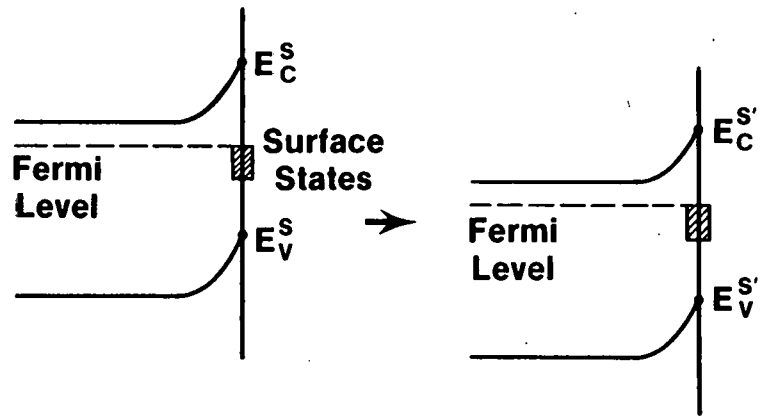
Exoergic Photoelectrosynthesis

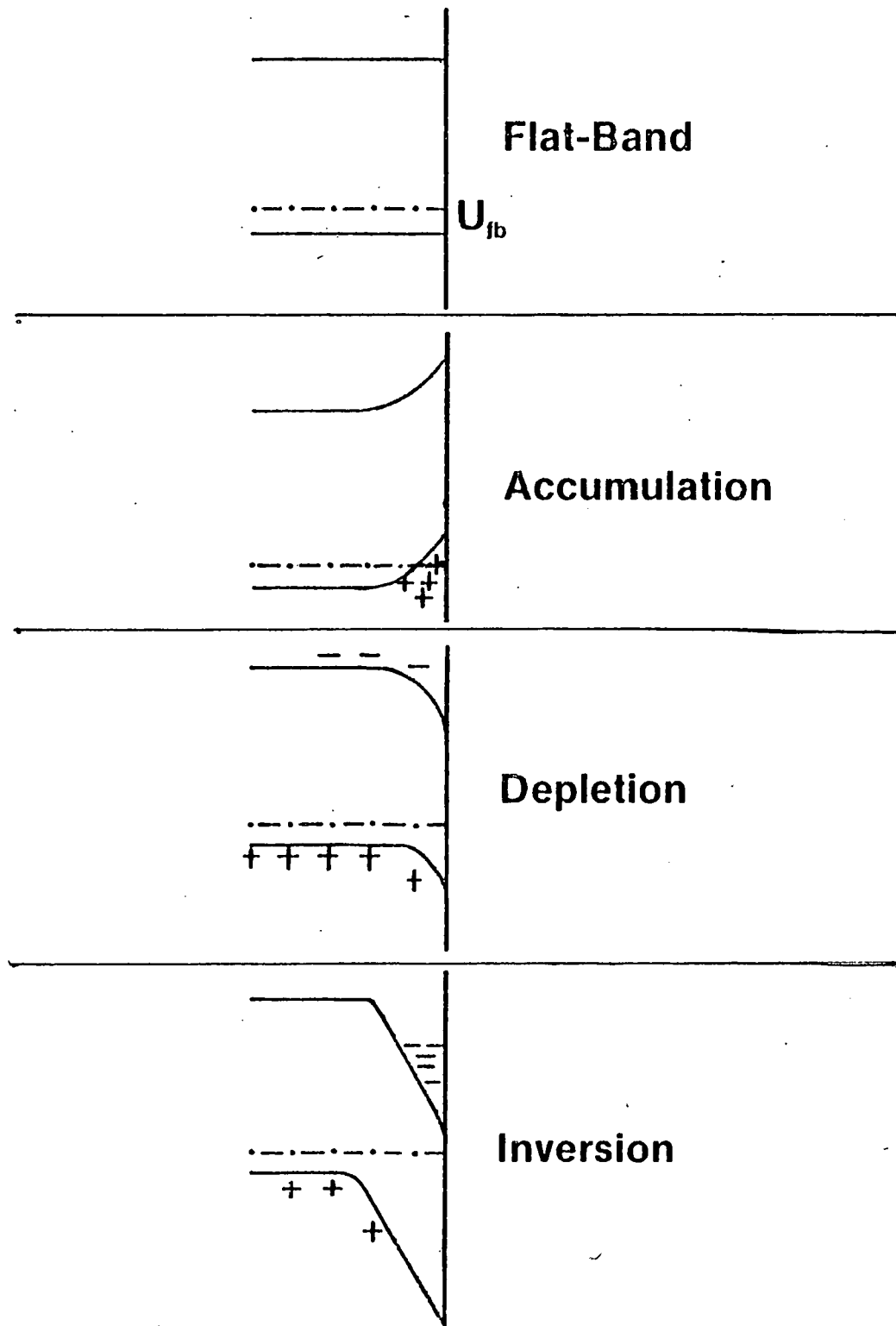
Chemical reaction is driven downhill in energy.

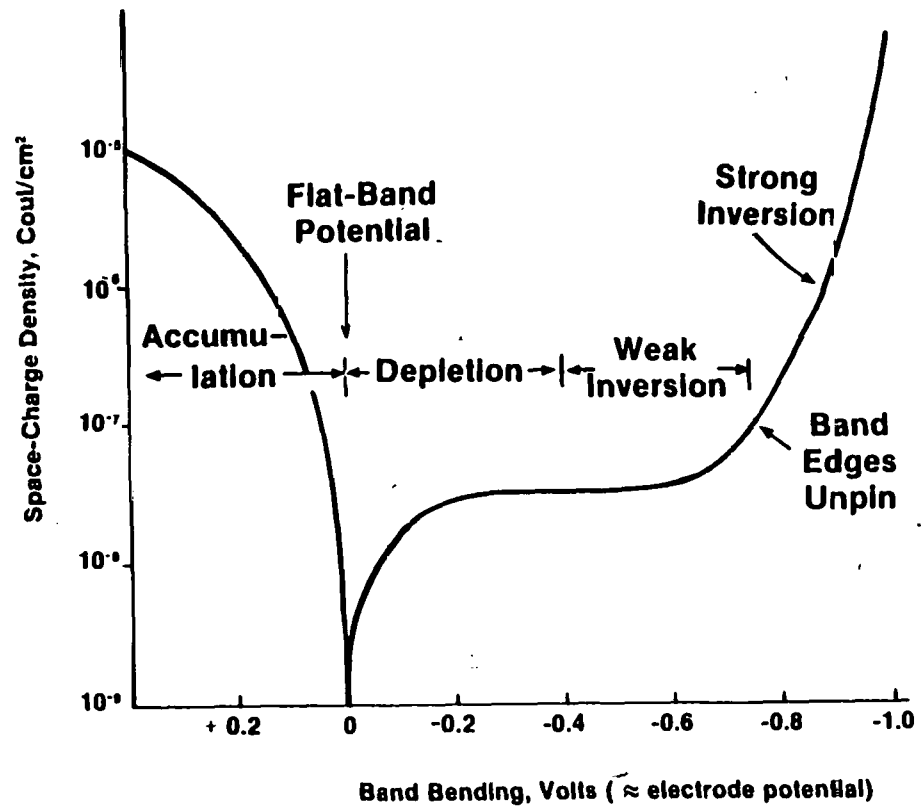
Endoergic Photoelectrosynthesis

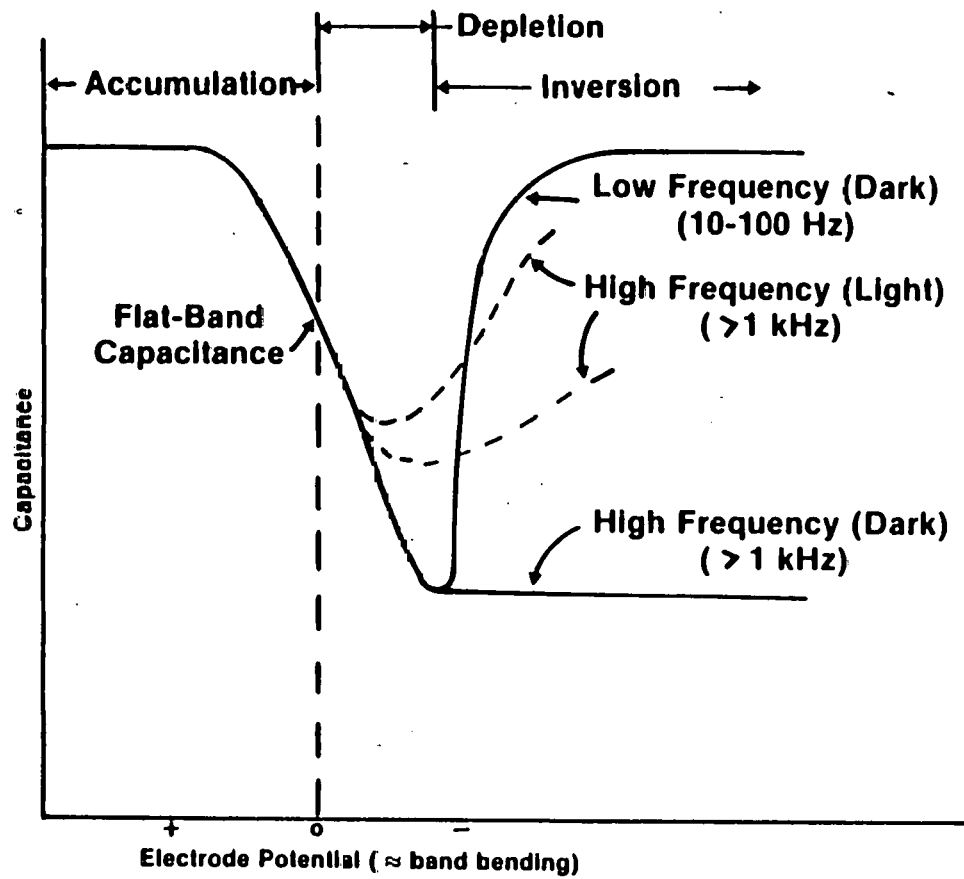
Chemical reaction is driven uphill in energy.

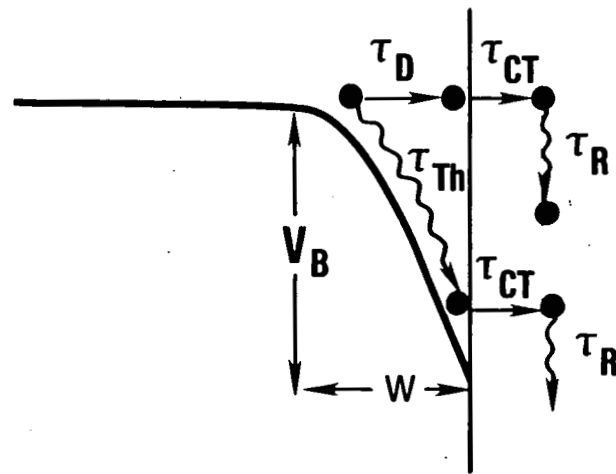






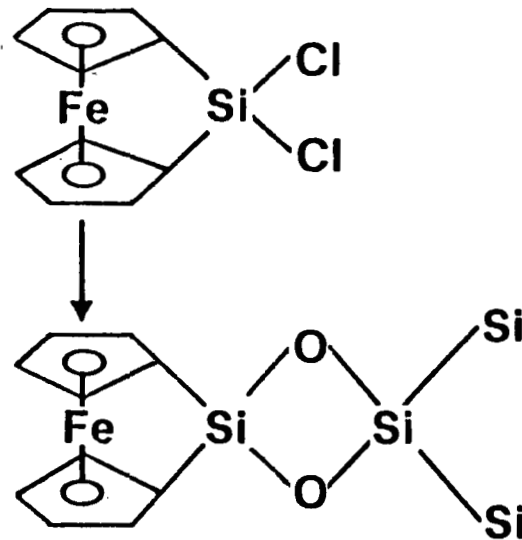
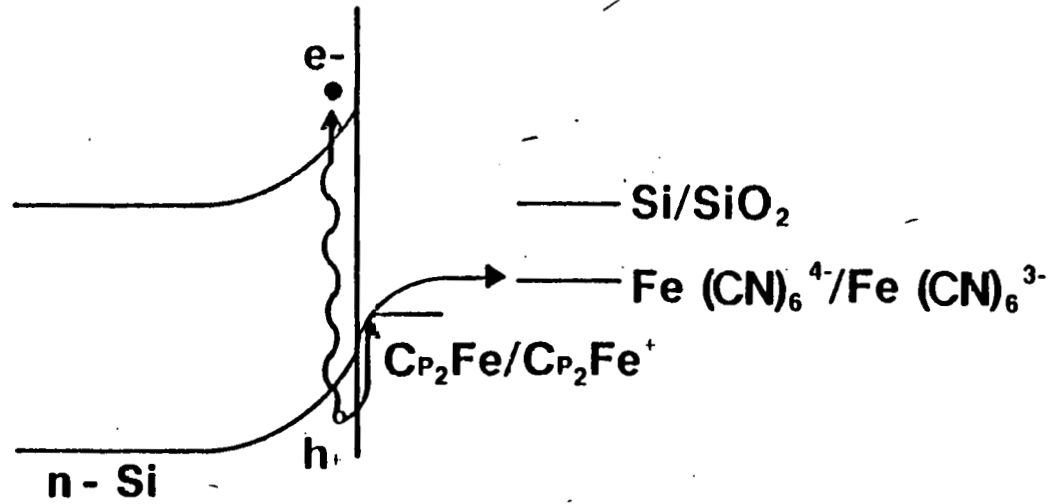




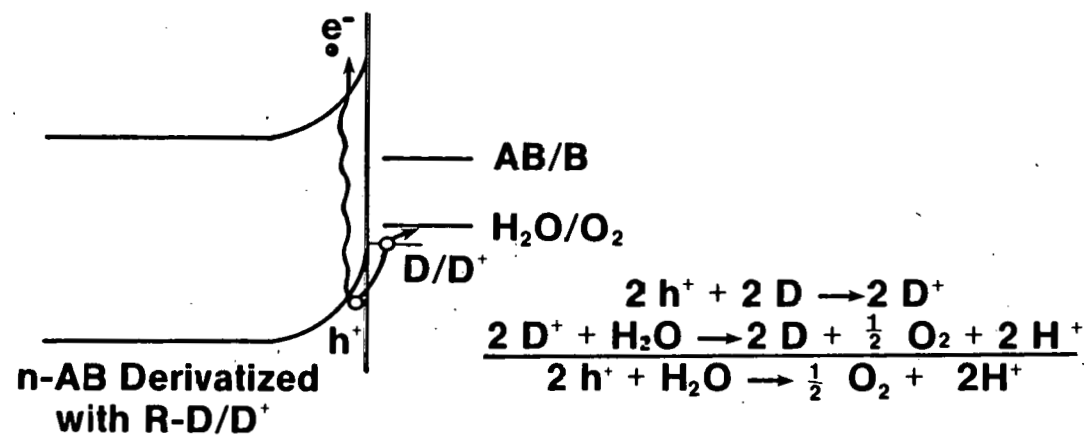
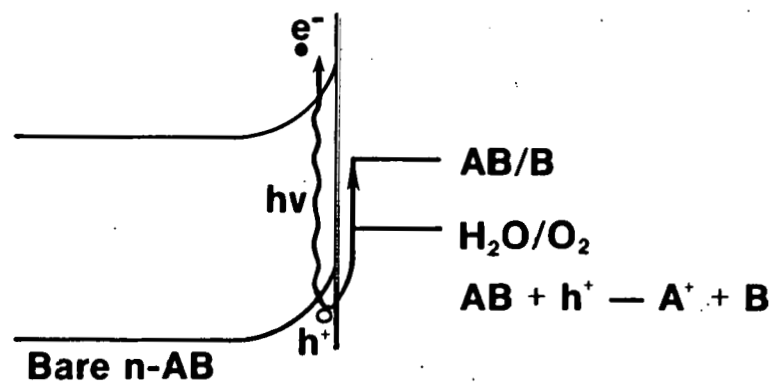


For Hot Electron Injection: $\tau_{Th} > \tau_D, \tau_{CT}, \tau_R$

Derivatized Silicon



Derivatized Electrodes (for stability)



Dye Sensitization

