

# Semiconductor Particles and Arrays for the Photoelectrochemical Utilization of Solar Energy

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The principles of the design of integrated chemical systems based on semiconductor materials for the photoelectrochemical utilization of solar energy to drive useful chemical reactions are described. The use of different support materials, such as Nafion and silica, to prepare particulate systems is discussed. Systems with very small ("Q-") particles are described. Charging of these particles is proposed as an important factor in the determination of particle energetics (optical band gap and potentials of photogenerated electrons and holes). Semiconductor arrays, with a number of junctions in series to provide higher driving potentials, are discussed, and two systems for the photosplitting of water to hydrogen and oxygen are described.

For about the last seventeen years, there have been worldwide efforts to develop photoelectrochemical (PEC) systems based on semiconductor materials for the utilization of solar energy to drive chemical reactions. This work has been the subject of many reviews and monographs [1-13], which document the basic principles of such systems, and describe the progress in this field and the problems associated with the fabrication and application of PEC devices. Thus no attempt will be made here to provide a detailed review of this field or discuss details of the principles of semiconductor electrode behavior. Rather, this paper will stress the "inte-

grated chemical system" (ICS) approach to the construction of PEC systems and discuss some recent work in this area, mainly by groups at The University of Texas, on supported particle systems and multielectrode arrays.

## 1. Integrated Chemical Systems

An ICS is a heterogeneous, multiphase system containing different components (usually of the size of 0.1 to several  $\mu\text{m}$ ), designed and arranged for specific functions or to carry out specific processes [14]. The different components, such

as semiconductor particles, polymer supports, catalyst materials, etc., will often have a particular structure and organization to improve the performance of the system and promote synergistic behavior. A number of ICS have been described and the general principles of construction and means of characterization considered [15]. Typical components of ICS and methods of construction are given in Tables 1 and 2. Indeed, the structure employed in biological photosynthesis generally follows this ICS form, with the relevant pigments, relays, and enzyme redox catalysts supported in a thylakoid membrane. The design of systems for carrying out artificial photosynthetic processes also generally follows this ICS approach [1, 6, 16].

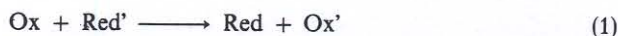
Table 1  
Components of Integrated Chemical Systems

1. Supports	Insulators Electronically conductive Polymers Membranes and L-B films Clays and zeolites
2. Catalysts	Metals Metal oxides Organometallic Enzymes and modified enzymes
3. Charge carriers (mediators, relays)	Redox couples Conductive polymers
4. Linking and coupling agents	
5. Photoactive centers	Semiconductors Chromophores
6. Chemically sensitive and selective centers	

Table 2  
Methods of Construction of Integrated Chemical Systems

1. Electrodeposition (metals, polymers, semiconductors)
2. Photodeposition
3. Etching (chemical, electrochemical, photo-)
4. Chemical synthesis and deposition
5. Spin coating and photolithography
6. Plasma deposition
7. Chemical vapor deposition
8. Vacuum evaporation
9. Molecular beam epitaxy

Consider the general components of an ICS for the PEC utilization of solar energy to drive a chemical reaction



and shown schematically in Fig. 1 [6]. Some typical half-reactions of interest in PEC systems are shown in Table 3. The overall reactions can be classified [1] as either photosynthetic, when the reaction is not thermodynamically spontaneous in the dark (e.g.,  $\text{H}_2\text{O} \rightarrow \text{H}_2 + 1/2 \text{O}_2$ ), or photocatalytic, when  $\Delta G^0 < 0$  (e.g.,  $\text{CH}_3\text{COOH} \rightarrow \text{CO}_2 + \text{CH}_4$ ). The different steps suggested in the diagram are probably carried out most efficiently with different components. The

incident light is absorbed in the semiconductor material to form an electron ( $e^-$ )-hole ( $h^+$ ) pair. The support for the semiconductor and associated components can play an important role in providing the environment for maximizing the efficiency of  $e^-h^+$  production and maintaining the desired semiconductor structure, as discussed below. An electric field is frequently established in the interfacial region near the semiconductor surface; this assists in the separation of the  $e^-h^+$  pair, minimizing losses due to recombination (Fig. 2). Thus the semiconductor material plays the important role of transducer, converting the radiant energy to an internal electric current flow that can be used to drive oxidation and reduction reactions. After  $e^-h^+$  separation, considerations generally involve those in other electrochemical systems, i.e., interfacial electron transfer (et) reactions, redox chemistry, and heterogeneous catalysis. Since the semicon-

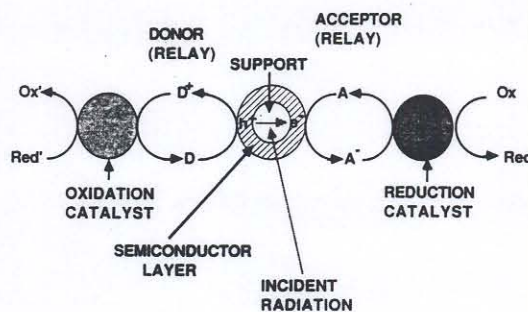


Fig. 1

Schematic of a generalized system for the utilization of solar energy to drive a reaction  $\text{Ox} + \text{Red}' \rightarrow \text{Red} + \text{Ox}'$  (for example  $2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2$ ). Light is captured in the semiconductor layer contained in a suitable support. The photogenerated electrons and holes ( $e^-$  and  $h^+$ ) are captured by the relays A and D, respectively. The species  $A^-$  and  $D^+$  are produced and used, in conjunction with suitable catalysts, to drive the final reaction

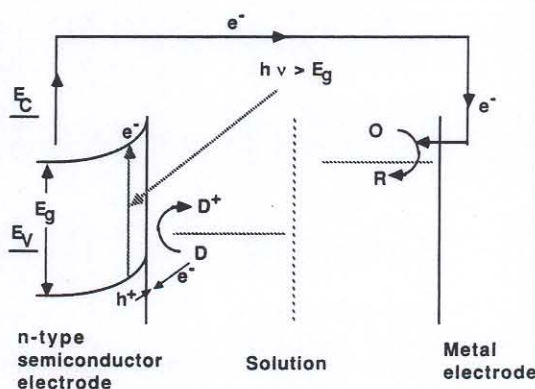


Fig. 2

Schematic representation of an illuminated n-type semiconductor immersed in a solution containing the  $D^+$ , D redox couple and connected to a metal electrode contacting a second solution containing the O, R redox species. The two solutions are connected by an ionic conductor (e.g. a membrane or salt-bridge). The band-bending in the semiconductor represents the electric field that forms at the semiconductor/solution interface.  $E_V$  and  $E_C$  are the energies of the valence and conduction band edges, respectively; on the scale of potentials vs. N.H.E., these would be about +3.0 V and 0 V for  $\text{TiO}_2$  (rutile) in a solution at pH 0. This PEC cell carries out the overall reaction  $\text{D} + \text{O} \rightarrow \text{D}^+ + \text{R}$  under illumination

ductor surfaces generally are not good catalytic ones for the ultimate et reactions (e.g., hydrogen or oxygen evolution), the strategy frequently adopted involves capturing  $e^-$  and  $h^+$  in rapid et reactions with appropriate couples (called mediators or relays) and placing heterogeneous et catalysts on or near the semiconductor surface. Several ICS designed along the lines of this scheme will be described below.

Table 3  
Typical Half-Reactions in Photoelectrochemistry

Reductions			Oxidations		
Ox	Red	Application	Red'	Ox'	Application
H <sup>+</sup>	H <sub>2</sub>	Fuel Generation	Cl <sup>-</sup>	Cl <sub>2</sub>	Disinfection
CO <sub>2</sub>	CH <sub>4</sub>	Fuel Generation	Br <sup>-</sup>	Br <sub>2</sub>	Energy Storage
Cu <sup>2+</sup>	Cu	Metal Removal	Organic	CO <sub>2</sub>	Pollution Control
Ag <sup>+</sup>	Ag	Metal Recovery	CN <sup>-</sup>	CNO <sup>-</sup>	Pollution Control
Pt(IV)	Pt	Catalyst Preparation	H <sub>2</sub> O	O <sub>2</sub>	Sacrificial Donor
O <sub>2</sub>	H <sub>2</sub> O <sub>2</sub>	Synthesis	CH <sub>3</sub> CO <sub>2</sub> <sup>-</sup>	CO <sub>2</sub> , CH <sub>4</sub>	Synthesis

## 2. Particle Systems

The simplest semiconductor ICS are probably those based on particles. While the earliest systems simply involved irradiation of particle dispersions, such as TiO<sub>2</sub> and CdS [17], later systems utilized Pt or other catalysts to assist in the et reactions [18–20]. Such systems can be roughly considered as short-circuited PEC cells, where the photodriven redox reactions occur on the semiconductor and catalyst surfaces [1]. Because these usually consist of particles whose dimensions are small compared to the typical widths of space charge layers for the low doping levels within the particles, it is unlikely that electric fields within the particles play a major role in promoting  $e^-h^+$  separation. However fields may exist because of specific ionic adsorption on the particle surface. Charges may also be trapped at surface sites; for example the absorbed photon at a Ti(IV)-OH<sup>-</sup> center can be considered as a ligand-to-metal (L-M) transition to produce Ti(III) OH•, followed by rapid reaction of the hydroxyl radicals. Such particulate systems have been, and continue to be, the subject of many investigations; some typical reactions carried out at irradiated particles are listed in Table 4. Physical characterization of such particle systems have utilized electrochemical [21–25], electrophoretic [21], photochemical [20, 26, 27], electron spin resonance [28], and luminescence [29, 30] methods, as well as X-ray diffraction, photothermal and photoacoustic spectroscopy, surface spectroscopy, and microscopic methods.

Semiconductor particles or films formed on a variety of support materials have also been studied. The support material can provide several advantages. It prevents flocculation and settling of small particles. If the support is a transparent core upon which a thin semiconductor film or very small particles are formed, losses due to  $e^-h^+$  recombination inside the particles (at distances larger than the diffusion length of the carriers) can be minimized. The support can also provide a fixed bed of small particles for use in photoreactions with a flowing stream. The major point of interest here, however, is the use of the support as a matrix for construction of an ICS and as a means of controlling

Table 4  
Representative Photoreactions at Particulate Semiconductors

Reactants	Products	Semiconductors	Refs.
CN <sup>-</sup> , O <sub>2</sub>	CNO <sup>-</sup>	TiO <sub>2</sub> , CdS, ZnO	<sup>1)</sup>
CO <sub>2</sub> , H <sub>2</sub> O	CH <sub>3</sub> OH, HCHO	TiO <sub>2</sub> , CdS, GaAs	<sup>2)</sup>
CH <sub>4</sub> , NH <sub>3</sub> , H <sub>2</sub> O	Amino acids	Pt/TiO <sub>2</sub>	<sup>3)</sup>
Many organics, H <sub>2</sub> O	H <sub>2</sub> , CO <sub>2</sub>	Pt/TiO <sub>2</sub>	<sup>4)</sup>
Many organics, O <sub>2</sub>	H <sub>2</sub> O, CO <sub>2</sub>	Pt/TiO <sub>2</sub>	<sup>5)</sup>
CH <sub>3</sub> COOH	CH <sub>4</sub> , CO <sub>2</sub>	Pt/TiO <sub>2</sub>	<sup>6)</sup>
N <sub>2</sub> , H <sub>2</sub> O	NH <sub>3</sub>	TiO <sub>2</sub> , WO <sub>3</sub> , Fe <sub>2</sub> O <sub>3</sub>	<sup>7)</sup>
Ph <sub>2</sub> C=CH <sub>2</sub> , O <sub>2</sub>	Ph <sub>2</sub> C=O	TiO <sub>2</sub>	<sup>8)</sup>
H <sub>2</sub> S	H <sub>2</sub> , S	Pt/CdS, RuO <sub>2</sub> /CdS	<sup>9)</sup>

<sup>1)</sup> S. N. Frank and A. J. Bard, *J. Phys. Chem.* **81**, 1484 (1977).

<sup>2)</sup> a) T. Inoue, A. Fujishima, S. Konishi, and K. Honda, *Nature* **277**, 637 (1979); b) M. Halman and B. Ourian-Blajeni, *ibid.* **275**, 115 (1978).

<sup>3)</sup> a) W. W. Dunn, Y. Aikawa, and A. J. Bard, *J. Am. Chem. Soc.* **103**, 6893 (1981); b) H. Reiche and A. J. Bard, *ibid.* **101**, 3127 (1979).

<sup>4)</sup> T. Kawai and T. Sakata, *Chem. Phys. Lett.* **80**, 341 (1981); *ibid.* *Nouv. J. Chim.* **5**, 279 (1981).

<sup>5)</sup> I. Izumi, W. W. Dunn, K. Wilbourn, F. R. Fan, and A. J. Bard, *J. Phys. Chem.* **84**, 3207 (1980).

<sup>6)</sup> B. Kraeutler and A. J. Bard, *J. Am. Chem. Soc.* **100**, 5985 (1978).

<sup>7)</sup> a) G. N. Schrauzer and T. D. Guth, *J. Am. Chem. Soc.* **99**, 7189 (1977); b) E. Endoh, J. K. Leland, and A. J. Bard, *J. Phys. Chem.* **90**, 6223 (1986).

<sup>8)</sup> a) M. A. Fox and C. C. Chen, *J. Am. Chem. Soc.* **103**, 6757 (1981); b) Other applications to organic synthesis are reviewed in M. A. Fox, *Accs. Chem. Res.* **16**, 314 (1983).

<sup>9)</sup> a) A. J. Nozik, *Appl. Phys. Lett.* **30**, 567 (1977); b) E. Borgarello, K. Kalyanasundaram, and M. Grätzel, *Helv. Chim. Acta* **65**, 243 (1982); c) M. Matsumura, Y. Saho, and H. Tsubomura, *J. Phys. Chem.* **87**, 3807 (1983).

particle size. An example of an ICS for the photogeneration of hydrogen, as shown on the right side of Fig. 1, is based on CdS particles precipitated in a Nafion matrix [14b, 31]. The basic concept is given in Fig. 3. Nafion<sup>TM</sup>, a perfluorinated sulfonate cation exchange membrane produced by DuPont, serves as the support material and provides a means of assembly of the ICS. CdS is precipitated in the Nafion by either first treating it with Cd<sup>2+</sup> and then with H<sub>2</sub>S, or by clamping the Nafion membrane between a solution containing Cd<sup>2+</sup> and another containing sulfide ion. This latter method provides for the formation of a well-defined layer of CdS within the membrane. The ion-exchange sites in the membrane can then be used to incorporate suitable cationic redox species, such as methyl viologen (MV<sup>2+</sup>). The photoreaction within such a membrane can be demonstrated by immersing the Nafion/CdS/MV<sup>2+</sup> system in a solution containing a suitable reactant for the photogenerated holes (e.g., sulfide or tartrate ions) and irradiating it. Under irradiation the yellow membrane turns deep blue, demonstrating the formation of MV<sup>•+</sup> [13, 14b]. The hydrogen generation system requires the incorporation of a catalyst to promote the reaction between MV<sup>•+</sup> and protons. Particles of Pt serve this purpose, and can be incorporated into the film by soaking it in a Pt(NH<sub>3</sub>)<sub>2</sub>I<sub>2</sub> solution followed by treatment with NaBH<sub>4</sub> [32], or by photodeposition techniques [33]. With this ICS, Nafion/CdS/MV<sup>2+</sup>/Pt, hydrogen evolution occurs when the membrane is irradiated while in contact with a suitable electron donor, such as a sulfide. Larger particles of CdS can also be affixed in a support in a configuration where each particle contacts both sides of the membrane (monograin membranes); these can also be loaded with catalyst and evolve hydrogen [34].

A number of other supports have been tried with semiconductor photoelectrochemical systems; some examples are given in Table 5.

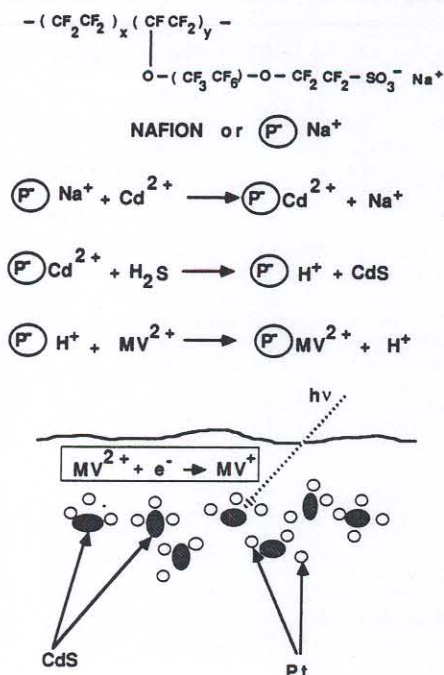


Fig. 3

Schematic representation of preparation of Nafion/CdS/Pt ICS [14b, 31]. Nafion is treated with  $\text{Cd}^{2+}$ , then with  $\text{H}_2\text{S}$  to precipitate CdS. Methyl viologen ( $\text{MV}^{2+}$ ) is incorporated by ion exchange and Pt by reduction of a suitable Pt species. Upon irradiation of the CdS, the photogenerated  $e^-$  reacts with  $\text{MV}^{2+}$  to form  $\text{MV}^+$ , which, in the presence of Pt, reduces  $\text{H}^+$  to hydrogen. The photogenerated  $\text{h}^+$  reacts with sulfide or another sacrificial electron donor

Table 5

Supports for Semiconductor Integrated Chemical Systems

1. Polymer films (Nafion, cellulose, Nylon)
2. Silica (particles, porous Vycor)
3. Clay
4. Zeolites
5. Micelles and vesicles
6. L-B films and bilayer membranes

### 3. Q-Particles

The support can also be used to form very small semiconductor particles that have properties that differ from those of the bulk material. There have been a number of recent studies of particles whose diameters are typically  $\sim 2\text{--}10\text{ nm}$ , that show an optical band gap,  $E_{g,\text{opt}}$ , that is larger than the band gap of the bulk material,  $E_g$  [35]. Such "quantum-" or "Q-particles" have been prepared from many semiconductor materials, e.g.,  $\text{CdX}$ ,  $\text{ZnX}$ ,  $\text{HgSe}$ ,  $\text{PbSe}$ ,  $\text{Cd}_3\text{P}_2$ ,  $\text{Cd}_3\text{As}_2$ ,  $\text{Zn}_3\text{P}_2$ ,  $\text{WO}_3$ , and  $\text{Si}$  ( $\text{X}=\text{S}, \text{Se}$ ) by formation under closely controlled solution conditions, frequently with the addition of agents, such as metaphosphate, that prevent flocculation. The support can also assist in the fabrication and stabilization of Q-particles. An interesting example of

this approach is that of Wang and Herron [35e], who used zeolite Y (Z-Y) as a support. Exposure of the Z-Y, which is a cation exchange material, to a solution of  $\text{Cd}^{2+}$ , followed by calcination at  $450^\circ\text{C}$  and gas phase treatment with  $\text{H}_2\text{S}$ , produced CdS that was contained only in the small sodalite cages of Z-Y. Under these conditions CdS particles with an absorption edge shifted into the ultra-violet region (compared to the bulk material or  $\mu\text{m}$  particle edge at ca.  $540\text{ nm}$ ) that consisted of only 4 CdS molecules, were produced. Additional examples of such supported Q-particles, based on recent work in our laboratories, involve the use of Nafion and Langmuir-Blodgett films as supports. For example, although precipitation of semiconductor particles from aqueous solutions in Nafion films, as discussed earlier, produces  $\mu\text{m}$ -size particles with energy levels characteristic of the bulk material, the use of nonaqueous solvents or gas phase treatments yield considerably smaller particles. Examples of CdS and CdSe in Nafion, taken from the work of Solomon et al. [36] are shown in Figs. 4 and 5. Note the large differences in absorbance edges for the different preparation conditions. With the Z-Y prepared CdS, treatment with water causes the particles to grow [35e]. A similar effect is found for the particles formed in Nafion.

A different approach to the production of a structured assembly of Q-particles involves the use of Langmuir-Blod-

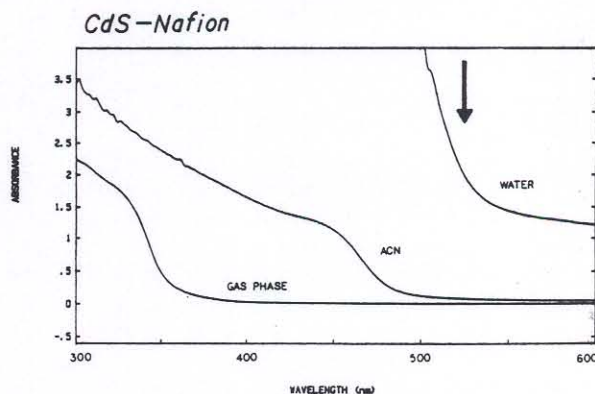


Fig. 4

Absorption spectra of CdS formed in a Nafion membrane under different conditions [36]

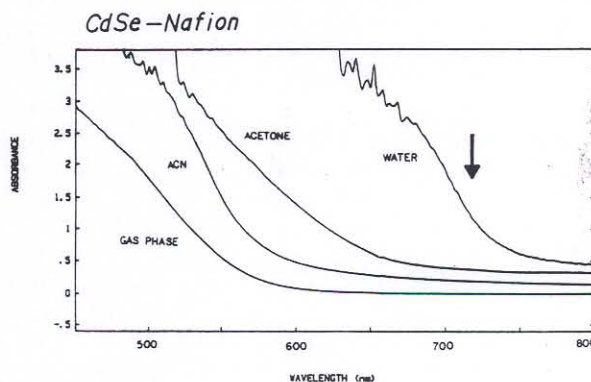


Fig. 5

Absorption spectra of CdSe formed in a Nafion membrane under different conditions [36]

gett (L-B) films as templates [37]. For example a film of cadmium arachidate can be formed at the water/air interface with a film balance and then transferred, at constant surface pressure, as an organized monolayer assembly, to a glass plate, by well-developed L-B techniques [38]. Treatment of this film with  $H_2S$  produces a thin layer of CdS particles which show an absorbance edge that is displaced by about 0.38 eV from that of bulk CdS (Fig. 6). The same procedure can be used to form multilayer structures, with up to seven layers of arachidic acid transferred to the glass plate. The fact that all of the films show the same absorbance edge suggests that the particle sizes of each layer are about the same and that there are no strong electronic interactions between layers. Yet one more approach to supported Q-particles involves attachment of a monolayer of a reactant to the surface of a silica particle, followed by washing and treatment with a suitable reagent to form the desired semiconductor material. For example 0.18  $\mu m$  silica particles treated with  $WCl_6$  in  $CH_2Cl_2$ , followed by washing and treatment with water, form thin (Q-) layers of  $WO_3$  on the  $SiO_2$  [39].

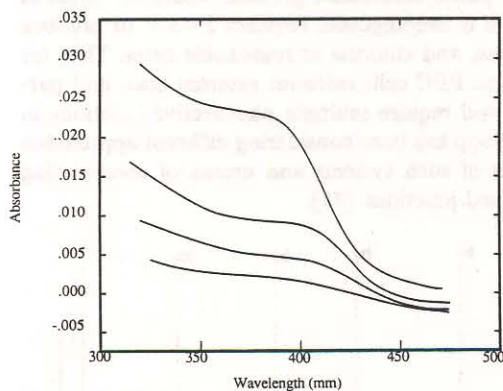


Fig. 6

Absorption spectra of CdS formed in cadmium arachidate Langmuir-Blodgett films of (1) 1, (2) 2, (3) 3, and (4) 7 layers [37]. Bulk CdS shows an absorption onset at about 520 nm

#### 4. Particle Charging Effects

The radiation that is absorbed by bulk semiconductors and large particles is determined by  $E_g$ . The energies of the photogenerated electrons and holes, which govern the nature of the redox reactions that can be driven at the irradiated particles, are based on the locations of the semiconductor conduction and valence band edges,  $E_C$  and  $E_V$ , respectively. These energies can be obtained by electrochemical measurements, for example, by determining what half-reactions can be photodriven at a given semiconductor and measurement of the redox potential associated with that half-reaction [21–25]. For Q-particles, the particle energetics are different than those for the bulk material. As mentioned above, the optical band gap,  $E_{g,opt}$ , is larger than  $E_g$ , and increases with a decrease in the particle radius,  $R$ . This effect has been treated by a “particle-in-a-sphere” model [35a, 40], which leads to the approximate relation:

$$E_{g,opt} = E_g + \frac{h^2}{8R^2} \left[ \frac{1}{m_e} + \frac{1}{m_h} \right] - \frac{e^2}{\epsilon R} + \text{polarization terms}, \quad (2)$$

where  $e$  is the electronic charge,  $m_e$  and  $m_h$  are effective masses of  $e^-$  and  $h^+$ , and  $\epsilon$  is the dielectric constant. Basically this equation describes how the properties of the particles deviate from those of a bulk structure with well-developed bands, when the particle dimensions begin to approach molecular dimensions. Recent research in our laboratories suggests that excess charge on the semiconductor particles can also affect  $E_{g,opt}$  and the  $e^-$  and  $h^+$  energies [41]. The model used is based on the effect of electron concentration and the onset of degeneracy on the optical transitions and location of the Fermi level in bulk semiconductors [42]. For example, for bulk InSb the absorption edge of a highly-doped ( $5 \cdot 10^{18}$  electrons/cm<sup>3</sup>) n-type sample lies at 3.2  $\mu m$ , compared to that of an intrinsic sample at 7.2 eV. The concept of the “Burstein shift”, used to explain this difference [43], can also be applied to small semiconductor particles. This model predicts that  $E_{g,opt}$  and the band edge locations depend upon the electron density in the particles,  $n$ , where  $n = \Delta n/V = \Delta n/(4\pi R^3/3)$ , and  $\Delta n$  is the excess number of electrons in a particle:

$$E_{g,opt} = E_g + [1 + (m_e/m_h)] [E_f - E_C - 4kT] \quad (3)$$

$$E_f - E_C = (h^2/2m_e)(3n/8\pi)^{2/3}, \quad (4)$$

where  $E_f$  is the energy of the Fermi level. Conceptually, as the electron density in the particle increases, the Fermi level moves into the conduction band. Under these conditions, the vertical transition from the filled valence band to the lowest unfilled level in the conduction band is larger than  $E_g$ , and the energy of the excited electron is higher than  $E_C$ . This occurs when  $n > n_{crit}$ , where  $n_{crit}$  is the value of  $n$  when  $E_f - E_C = 4kT$ . For very small semiconductor particles this occurs when only a few extra electrons are produced in the particle. Representative results for CdS particles are shown in Figs. 7 and 8 [41]. Note, for example, that only 0.1 ad-

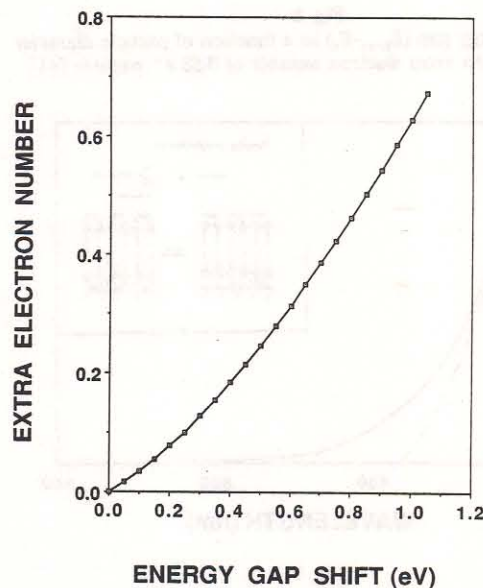


Fig. 7

Dependence of energy gap shift ( $E_{g,opt} - E_g$ ) on number of extra electrons in CdS semiconductor particle of diameter, 15 Å [41]

ditional electron in a particle of 15 Å diameter can lead to a shift in the absorption edge of 0.25 eV. This model can account for the absorption edge shifts observed when small particles are irradiated with intense light sources. For example, irradiation of 30 Å CdS particles with a 10 μs photoflash causes a reversible decrease in the absorbance in the 450–500 nm region immediately after the flash [26]. This can be interpreted by the above model by a photoflash-induced increase in electrons (and holes). When the irradiation is carried out in the presence of a sacrificial donor, like cysteine, which captures the holes produced upon irradiation, the flash-induced perturbation of the absorption spectrum lasts longer, since the rate of relaxation of the excess electrons is decreased. An analogous experiment can be carried out with the L-B layer CdS films described above (Fig. 9). When the film is irradiated with a 1000 watt tungsten-halogen lamp, the absorption edge shows a blue shift. When the irradiation beam was extinguished, the spectrum returned to the original one, showing that the shift could not be attributed to irreversible degradation of the

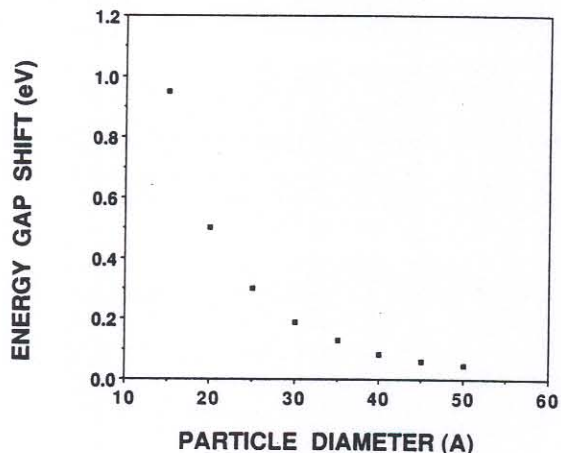


Fig. 8

Increase in energy gap ( $E_{g,opt} - E_g$ ) as a function of particle diameter for CdS with an extra electron number of  $0.58 e^-/\text{particle}$  [41]

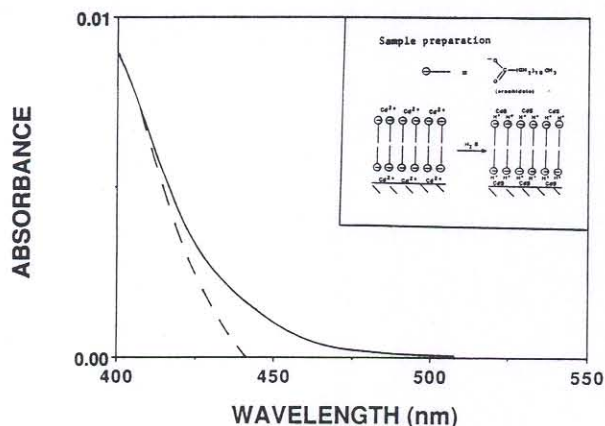


Fig. 9

Absorption spectra of CdS thin film array prepared by Langmuir-Blodgett technique with 7 cadmium arachidate layers. (—) with and (---) without irradiation with 1000 watt tungsten-halogen lamp

CdS particles. Charging effects can also cause the energies of the photogenerated electrons to be higher (i.e., the redox potentials to be more negative) and can account for the observation of redox processes occurring on particles that would not be predicted to occur based on values of  $E_C$  obtained from bulk semiconductor measurements [21]. Indeed this concept suggests that particle charging, especially under intense light or in the presence of sacrificial donors, will continue until some reaction of the photogenerated electrons occurs. Note also that exactly parallel effects will occur for excess holes in the valence band, which produce degenerate p-type materials, especially in the presence of sacrificial acceptors.

### 5. Semiconductor Arrays

One problem with the application of irradiated semiconductor/liquid junctions for driving useful chemical reactions is that the maximum photopotential developed across the junction is rarely greater than 0.8 V, and is more often below 0.6 V. Thus a single junction does not develop a sufficient driving force to carry out many reactions of interest. For example the photo-chloralkali process, where an aqueous brine solution is decomposed, requires 2–3 V to produce hydrogen, base, and chlorine at reasonable rates. Thus for most reactions, PEC cells (without external bias) and particulate ICS will require multiple photoactive junctions in series. Our group has been considering different approaches to the design of such systems and means of constructing series-connected junctions [45].

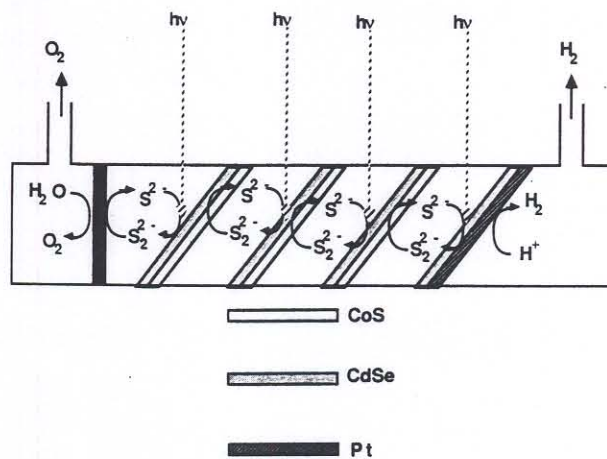


Fig. 10

Schematic diagram of multielectrode array of CdSe/CoS panels in cell for the photosplitting of water to hydrogen and oxygen without an external bias. All solutions contain 1 M NaOH. The internal solutions also contain 1 M S and 1 M  $\text{Na}_2\text{S}$

One approach has been the formation of  $\text{TiO}_2/\text{Pt}$  panels by the electrochemical anodization in 2.5 M  $\text{H}_2\text{SO}_4$  of 25 μm thick Ti foils after a layer of Pt (350 nm thick) has been deposited by sputtering. Such panels can then be arranged with intervening electrolyte solution layers (e.g.,  $\text{O}_2$ -saturated aqueous NaOH) in a series configuration to generate sufficient potential to drive the decomposition of water to  $\text{H}_2$  and  $\text{O}_2$  without the application of an external bias [45a]. This arrangement can also be employed with smaller band

gap semiconductors. For example, panels of CdSe/Ti/CoS can be formed and arranged as shown in Fig. 10 [45b,c]. The internal CdSe/S,  $S^{2-}$ , NaOH/CoS cells simply behave as photovoltaic cells (driving  $S^{2-}$  oxidation and S reduction without changes in the solution composition) and provide a bias for driving the reactions at the outer Pt electrodes. The outer electrodes drive the electrolysis of water and produce separated streams of hydrogen and oxygen. Note that this arrangement overcomes two difficulties that frequently arise in PEC cells: the unsuitable location of the valence (or conduction) band for the reaction of interest and the instability of the semiconductor under the conditions where the reactions of interest occurs [46]. For example  $E_v$  for CdSe is not located at a sufficiently positive potential to drive the oxidation of water to  $O_2$ . However the series combination provides sufficient bias to move the energy levels to the required locations. CdSe is also unstable when irradiated in a solution that does not contain a suitable stabilizing redox species, like  $S^{2-}$ , so that a biased CdSe electrode in NaOH solution would decompose under illumination. However in the series-cell arrangement, the water oxidation occurs at a stable Pt electrode surface, so these stability problems do not arise. Note that the Texas Instruments Solar Energy System (TISES), that is based upon small spheres of Si, utilizes this strategy, where panels of p/n spheres in series with n/p spheres produce the driving voltage needed to decompose HBr to  $H_2$  and  $Br_2$  [47]. Methods of arranging these panels in series to yield even higher voltages have been proposed [48]. The challenge is to construct true ICS, e.g., involving supported particles, that will have a structure with the same type of series arrangement to produce the needed high potentials. Once again a biological analogy comes to mind. Most organisms utilize the rather small potential ( $\sim 100$  mV) built up across a single membrane to provide nerve impulses and for muscle movement. However a few organisms, such as the electric eel, can form special organs (electrocytes) in which these membranes are connected in series to produce potentials of up to 600–700 V. Our goal is to produce an analogous ICS structure (the “photoelectrochemical eel”) to drive reactions of interest!

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