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POLYMER-MODIFIED ELECTRODES, CATALYSIS AND WATER-SPLITTING REACTIONS

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Summary

Highlights of results on surface modified CdS semiconductors in the presence and absence of an externally applied anodic bias are presented. At zero applied bias, the surface modification involved coating the faces of CdS with electrically conductive polypyrrole and catalytic dispersions of transition metals (Pt, Rh, RuO_2) immobilized in polystyrene films. The combination of polypyrrole and catalytic polystyrene films prevented photo-induced dissolution of CdS and catalyzed H_2 and O_2 evolution. The amount and composition of metal dispersed in the polystyrene coating and the hydrophobic nature of the films were important in achieving good catalytic activity and stability of the CdS semiconductor. Sorption processes, the electronic contact between the polymer and the semiconductor and the particular transition metal catalyst selected also influenced the net yield of H_2.

1. Introduction

The instability of narrow-bandgap n-type semiconductors to oxidative photodegradation and the poor catalytic properties of the semiconductor surface for many chemical reactions of importance are major scientific obstacles to the development of a practical photoelectrochemical solar cell. To protect the semiconductor surface from oxidative photodegradation a broad range of strategies have been used based on limiting contact with water, promoting rapid interfacial charge transfer to redox species or altering the interfacial energetics to disfavor electrode decomposition with respect to the desired redox reaction. The effectiveness of the approach depends on manipulation of both thermodynamic and kinetic factors. Methods for stabilizing the semiconductor–electrolyte interface have involved non-aqueous electrolytes [1], molten salts [2], high electrolyte concentrations [3], thin metal films [4], semiconductor–oxide layers [5], high concentra-

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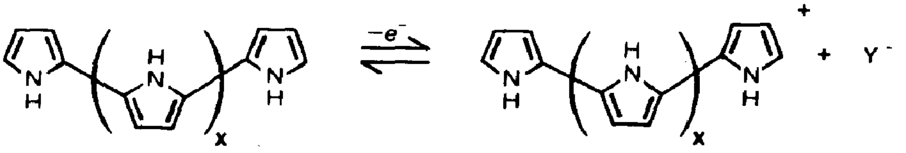
tions of oxidizable species [6] and adsorption and covalent attachment of charge mediators [7].

Recently we reported on a promising new approach to alleviate the photocorrosion reaction of photoanodes and to improve the surface kinetics for the oxidation of water [8 - 11]. The key component of this approach is an electrically conductive polymer film which works synergistically with the redox electrolyte and/or a catalyst to stabilize the semiconductor surface from photodegradation and to promote desired reactions at the electrode surface. Polypyrrole was selected as the electrically conductive polymer. This polymer is conductive in the oxidized state and is insulating in the neutral state [12].



Polypyrrole itself is a poor catalyst for oxygen evolution [13]. Normally the polymer film is unstable in aqueous electrolytes under oxidative conditions, such as at electrode potentials greater than 0.6 V *versus* SCE [14, 15]. Polypyrrole is water permeable since gas evolution takes place at the platinum–polymer interface. This results in the blistering of the film and its eventual detachment [14 - 16]. Electrocatalytic studies [13] combined with Auger depth-profile measurements have established, however, that oxygen evolution can be confined to the outermost surface of the polymer when a platinum layer 50 Å thick is argon ion-beam sputtered onto the surface of the film. Auger analysis of the thickest polypyrrole films where platinum was deposited on the surface indicated that the polymer was able to transmit charges over large distances exceeding 125 000 Å.

When CdS is coated with polypyrrole incorporating suitable transition metal dispersions, the photoinstability of the semiconductor is suppressed and its catalytic activity towards the oxidation of water is markedly improved [9 - 11]. Important factors that determine the effectiveness of the surface-modified CdS semiconductor to split water into H_2 and O_2 include the good charge transport property of polypyrrole, the nature and concentration of the catalytic dispersion, the water activity at the surface of the semiconductor, the pH and the absence or presence of an externally applied anodic bias. In this article highlights of these studies [8, 10, 11] and the limitations [9] associated with the derivatization are presented.

2. Experimental details

Oxides of ruthenium, platinum or rhodium powders were dispersed in a polymethacrylate based silver paint [8, 10] or a polystyrene film [11] affixed to the semiconductor surface. Only the less stable ⟨0001⟩ face (predominantly Cd atoms) of the single-crystal CdS was exposed to actinic light. A 250 W tungsten–halogen lamp with suitable interference filters and heatreflectance mirrors produced a band of radiation between 400 nm and 510 nm. Oxygen and hydrogen production were monitored with Clark-type gas sensors and gas chromatography. The concentration of Cd^{2+} ions produced during photocorrosion was determined by atomic absorption spectrophotometry. Electrochemical measurements were conducted with conventional instrumentation. The experimental details are given elsewhere [8 - 11].

3. Results and discussion

3.1. Suppression of photocorrosion of CdS at anodic bias

Cadmium sulfide has a bandgap of 2.4 eV with a valence band (1.4 V *versus* SCE) positive of the O_2/H_2O redox couple and a conduction band (—1.0 V *versus* SCE) negative of the H^+/H_2 couples [17]. Over a pH range of 0 - 13.6, the photogenerated holes and electrons are thermodynamically capable of oxidizing and reducing water simultaneously to produce hydrogen and oxygen.

$$4h^+ + 2H_2O \longrightarrow O_2 + 4H^+ \qquad (1)$$

$$2e^- + 2H_2O \longrightarrow H_2 + 2OH^- \qquad (2)$$

However, the oxidative decomposition reaction of CdS (eqn. (3)) occurs at about 0.06 V (SCE) in aqueous solution [17] and predominates over O_2 evolution when, under anodic bias, the electrode is illuminated with supra-bandgap energy light.

$$2h^+ + CdS \xrightarrow{H_2O} Cd^{2+}{}_{aq} + S \qquad (3)$$

Recently we investigated [8, 10] whether it was possible to stabilize anodically biased CdS against photo-induced dissolution and to permit the water oxidation reaction. Figure 1 is a conceptual model for achieving protection of CdS and the water-oxidation reaction. The surface of the semiconductor is coated with a highly conductive polymer film incorporating catalytically active metal centers. The rationale behind this approach is that the combination of a conductive polymer and a catalyst provides a mechanism for the rapid removal and trapping of photogenerated holes from the semiconductors and the catalytic oxidation of water to O_2. At the counter-electrode (not shown in the figure) the cycle is completed with the complementary H_2 production reaction.

To investigate the reasonableness of this model, studies [8, 10] were made of bare CdS electrodes, CdS coated with a catalyst, and CdS coated with polypyrrole containing a catalyst. The catalyst was RuO_2 powder dispersed in a thin layer of silver paint on the surface of either the bare electrode or the polypyrrole-covered electrode.

One aspect of this investigation correlated the amounts of O_2 and Cd^{2+} ions produced by each electrode after 50 C cm^{-2} had passed (Fig. 2). With no coating about 99% of the photogenerated holes that contributed to

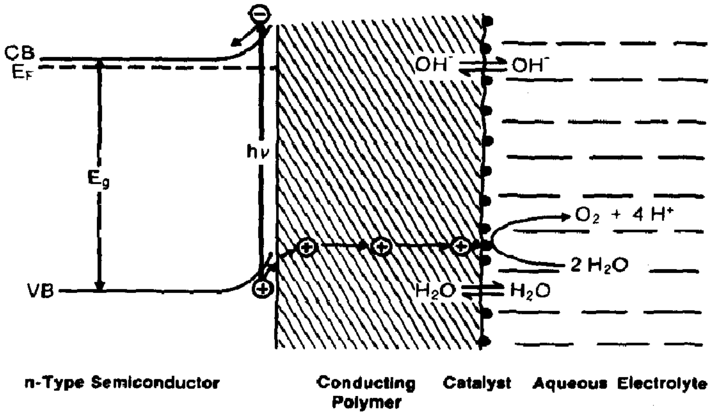


Fig. 1. Conceptual model for suppression of photodegradation of n-type semiconductor and promotion of the water oxidation reaction.

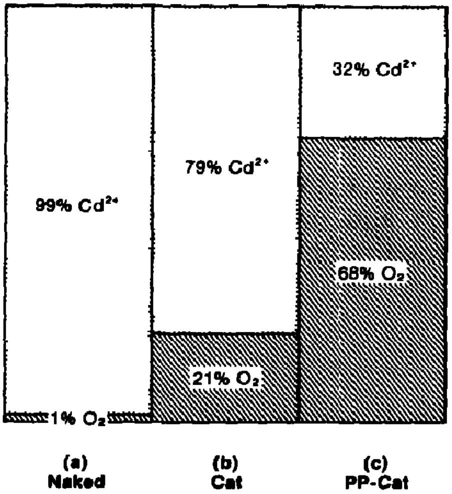


Fig. 2. The percentage of O_2 and Cd^{2+} ions produced from naked, catalyst-coated (Cat), and polypyrrole–catalyst-covered (PP–Cat) n-type CdS photoanodes in a 0.5 M Na_2SO_4 solution at pH 8.6 after 49 C cm^{-2} was passed. (Data from ref. 8.)

the photocurrent led to dissolution of CdS. With the addition of the catalyst, about 79% of holes reacted with CdS itself and 21% with water. When the CdS electrode was coated with polypyrrole which was overlayed with RuO_2, 68% of the holes were consumed in the O_2 evolution reaction and only 32% contributed to the destruction of the semiconductor lattice. These results indicate that polypyrrole films overlaid with ruthenium dioxide powder immobilized in silver paint greatly improve the stability of CdS photoanodes for the oxidation of water. However, the time profile for oxygen production exhibited an induction period due to the preferential oxidation of the silver [10]. To avoid this problem and to control the water activity of the electrode surface (see Section 3.2), hydrophobic films of polystyrene are more useful in affixing the catalyst to the surface of the semiconductor.

In part, the effectiveness of the polypyrrole film to extract holes from the CdS surface derives form the good transport property of the polymer and its large capacitance [16]. Polypyrrole can conduct holes over a wide range of potentials because the redox level of the polymer adjusts to match that of the redox electrolyte [10]. A comprehensive and critical review [10] of polypyrrole modified semiconductors has recently appeared.

3.2. *Photobehavior of CdS at zero applied bias*

The net product distribution for reactions (1) and (3) is expected to depend on the magnitude of the applied anodic bias. In this section, we present results on the photochemical behavior of surface modified CdS crystals suspended in aqueous solutions at zero applied bias [11]. The surface modification involved coating the faces of the crystals with polypyrrole and polystyrene films containing catalytic dispersions of transition metals (platinum, rhodium, RuO_2) as illustrated for one case in Fig. 3. Such a monolithic structure containing no external wires has been called a photochemical diode [18]. The polystyrene-immobilized catalysts do not physically contact the surface of the semiconductor. The junction characteristics of such surface modified CdS systems differ from those in which the catalyst are deposited directly on the surface of CdS [19 - 21]. Furthermore, the hydrophobic polystyrene films are expected to lower the water activity at the semiconductor surface resulting in a reduced solvation energy for dissolution of the semiconductor crystal lattice [11].

3.2.1. *Electrocatalysis*

Information on the surface coating was obtained from i–V curves (Fig. 4) for a bare graphite electrode and one coated with polypyrrole overlaid with RuO_2 powder (360 μg cm^{-2}) immobilized in polystyrene film 0.5 μm thick [11]. At the bare electrode, little anodic current was passed until the voltage exceeded 1.5 V (SCE). In contrast, the surface-modified graphite

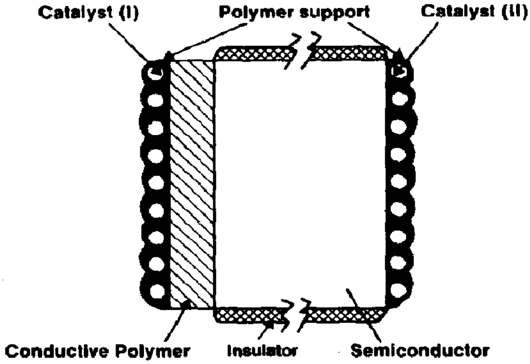


Fig. 3. Surface-modified photochemical diode: single-crystal CdS coated on one side with polypyrrole overlaid with RuO_2 powder immobilized in polystyrene film and on the other face with platinum black immobilized in polystyrene film.

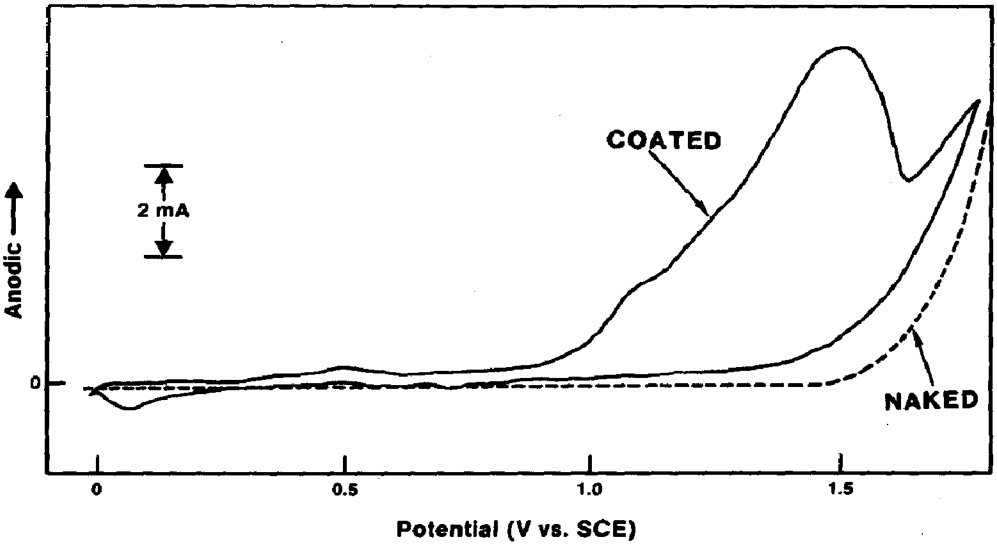


Fig. 4. Current–voltage curves for a naked graphite electrode (— — —) and RuO_2–polystyrene-coated polypyrrole film on a graphite electrode (———) in aqueous solution at pH 7.2 with 0.5 M Na_2SO_4. The electrode areas are 0.28 cm^2. The scan rate is 5 mV s^{-1}. (Data from ref. 11.)

electrode developed a current density of about 7.7 mA cm^{-2} at 1.1 V and O_2 bubbles evolved from the electrode surface. The *i–V* characteristics of the RuO_2–polystyrene–polypyrrole coated electrode are similar to those of a RuO_2 electrode with respect to the oxidation of water. At a fixed amount of RuO_2 powder (360 μg cm^{-2}), the current density doubled when the thickness of the polystyrene film was reduced from 5.0 to 0.5 μm. Conductivity of the dry film depended exponentially on the weight ratio of RuO_2-to-polystyrene. At the same weight ratio of metal-to-polymer, but with smaller particles, the conductivity of a platinum black-charged polystyrene film was two orders of magnitude higher than that of the RuO_2-loaded films. Conduction of charge by an electron-hopping mechanism between metallic particles in the polystyrene film was inferred. In contrast with the situation using metallated polystyrene films, increasing the thickness of the polypyrrole undercoating produced a higher current density.

3.2.2. Variation of surface coating on surface-modified CdS photochemical diode

Table 1 provides a comparison of product yields from various surface-modified CdS photochemical diodes illuminated with bandgap radiation (400 - 510 nm) for 40 h; the radiant power was 7.5 mW cm^{-2} after passing through the surface films [11]. Unavoidable air leaks in the photolysis vessel precluded quantitative measurement of O_2.

Illumination of the uncoated CdS crystal produced no H_2 or Cd^{2+} ions suggesting that the recombination of electron–hole pairs predominates. When the illuminated front surface was bare and the back surface was coated

TABLE 1

Comparison of H_2 and corrosion product (Cd^{2+}) yields from various surface-modified CdS photochemical diodes after 40 h illumination

Coatings[a]		*Products* (μmol)		
Front surface	*Back surface*	H_2	Cd^{2+}	*Conditions*
Bare	Bare	0	0	
Bare	Pt (0.5 μm PST)	0.4 (O_2 uptake)	0.1	1.0 M $LiClO_4$
RuO_2 (0.5 μm PST)	Pt (0.5 μm PST)	0.6	0	pH 11
PP–RuO_2 (0.5 μm PST)	Pt (0.5 μm PST)	2.6	0	25 °C
PP–RuO_2 (5.0 μm PST)	Pt (0.5 μm PST)	0.2	0	
PP–RuO_2 (0.5 μm PST)	InGa–Pt (0.5 μm PST)	3.5	0.5	
RuO_2 (0.5 μm PST)	Pt (0.5 μm PST)	1.3	0.3	1.0 M $LiClO_4$
RuO_2 (0.5 μm PST)	Pt (photodeposition)	2.7	0.1	pH 7.5
RuO_2 (0.5 μm PST)	Rh (0.5 μm PST)	4.9	0	25 °C

[a] Polystyrene (PST); polypyrrole (PP).

with polystyrene-immobilized platinum black (560 μg cm^{-2}), a net uptake of O_2 occurred with production of H_2 and Cd^{2+} ions. The uptake of O_2 suggests the reaction of conduction-band electrons with O_2 mediated by platinum particles in the polystyrene film.

$$Pt + e^- + O_2 \longrightarrow Pt + O_2^{-\cdot} \qquad (4)$$

Others have observed the photosensitized reduction of O_2 by CdS colloids and suspensions in the presence of platinum [22 - 24].

In some experiments (see Table 1) the coating on the back surface was held fixed and the components on the front surface were altered. For this situation, the most effective coating for H_2 production consisted of polypyrrole overlaid with RuO_2 powder dispersed in polystyrene 0.5 μm thick; 2.6 μmol H_2 were generated from water without evidence of photocorrosion. This amount of H_2 corresponds to about 10^4 monolayers of H_2. The device quantum yield near saturation for this particular case was estimated at 0.02; the theoretical device quantum yield for H_2 production is 0.5. Without polypyrrole present, but with the same RuO_2-polystyrene mixture, the H_2 yield decreased by a factor of 4. Lowering the concentration of RuO_2 powder by a factor of 10, even in the presence of polypyrrole, resulted in a decrease by a factor of 13 with respect to CdS coated with polypyrrole and RuO_2 powder in the polystyrene film 0.5 μm thick. Table 1 shows that the electronic contact on the back surface is important. An InGa ohmic contact on the back surface produced a 12% increase in H_2 yield compared with a photochemical diode without the ohmic contact when the amount of Cd^{2+} dissolved in solution is taken into account.

Table 1 shows that the amount of H_2 and Cd^{2+} ions generated at pH 7.5 when the catalyst on the back surface is varied and the coating on the front surface is held constant. Of the three catalyst coatings examined, rhodium black was the most effective for H_2 production compared with platinum black and the photodeposited platinum.

3.2.3 Further evaluation of the catalysts

The amount of H_2 detected depends not only on the water-cleavage and photocorrosion reactions, but also on the sorption processes [11]. A comparison of the H_2 uptake on platinum black and RuO_2 powder immobilized in polystyrene films showed that platinum black removed 25% - 30% of the H_2 introduced into the reaction vessel whereas the RuO_2 powder adsorbed only 0 - 4% of the H_2 over a 7 h period. Current–voltage curves provided further insight into differences among the platinum, RuO_2 and rhodium catalysts. Results of i–V measurements of graphite electrodes coated with a platinum black–polystyrene mixture indicated that the oxidized states of the platinum particle can act as sorption sites for H_2 or the reductive equivalents. Such sites can also act as recombination centers for electrons and holes. The existence of such states will affect adversely the net hydrogen yield. Furthermore, i–V data for a graphite electrode coated with the polymer-immobilized RuO_2 catalyst indicated that H_2 sorption on RuO_2 powder or the reductive equivalent is less favorable by 0.3 V than that on platinum black. However, the RuO_2 powder is a poorer catalyst for water reduction since the potential for H_2 production occurs a few tenths of a volt more negatively than is the case for platinum black. In the case of a graphite electrode coated with rhodium black dispersed in polystyrene, the potential corresponding to H_2 sorption on rhodium or the reductive equivalent was similar to that of RuO_2 powder; however, H_2 production took place at nearly the same potential as that of the platinum black. These results are consistent with the relatively large amount of H_2 produced from the CdS diode coated with rhodium black and suggest that it is a more effective catalyst for water reduction than platinum black. The data also suggest that the H_2 yields reported in Table 1 represent a lower limit. Other processes such as the reduction of polypyrrole may also reduce the net amount of H_2 produced although we have no evidence for this reaction.

In conclusion, surface modification of the CdS photochemical diodes with electrically conductive polypyrrole in combination with catalytic polystyrene films prevented photodegradation during the cleavage of water. Hydrophobic films of polystyrene are likely to have reduced $\Delta G_{\text{solvation}}$ for dissolution of CdS lattice and slowed the photocorrosion kinetics by retarding Cd^{2+} diffusion. The conductive polymer facilitated good electronic charge transport from the semiconductor to the catalytic particles. The amount and composition of the metal dispersed in the polystyrene films affected the charge transport and electroactivity of the polymer and consequently the stability and catalytic activity of the CdS semiconductor. Ohmic contact between the Pt–polystyrene film and CdS improved H_2 evolution kinetics. Polystyrene-immobilized dispersions of rhodium black were more effective for the catalytic production of H_2 from water than films containing platinum black or RuO_2 powder.

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References

1 H. S. White, F.-R. F. Fan and A. J. Bard, *J. Electrochem. Soc.*, *128* (1981) 1045.
W. Kautek and H. Gerischer, *Ber. Bunsenges. Phys. Chem.*, *84* (1980) 645.
L. F. Schneemeyer and M. S. Wrighton, *J. Am. Chem. Soc.*, *102* (1980) 6964.
M. Miyake, H. Yoneyama and H. Tamura, *Electrochim. Acta*, *22* (1977) 319.

2 P. Singh, R. Singh, K. Rajeshwar and J. Dubow, *J. Electrochem. Soc.*, *128* (1981) 1145.

3 F.-R. F. Fan, B. Wheeler, A. J. Bard and R. Noufi, *J. Electrochem. Soc.*, *128* (1981) 2042.
C. P. Kubiak, L. F. Schneemeyer and M. S. Wrighton, *J. Am. Chem. Soc.*, *102* (1980) 6898.

4 W. Gissler and A. J. McEvoy, in W. L. Wallace, A. J. Nozik, S. K. Deb and R. H. Wilson (eds.), *Photoelectrochemistry: Fundamental Processes and Measurement Techniques*, The Electrochemistry Society, Princeton, 1981, p. 212.
L. A. Harris and J. A. Hugo, *J. Electrochem. Soc.*, *128* (1981) 1203.
S. Menezes, A. Heller and B. Miller, *J. Electrochem. Soc.*, *127* (1980) 1268.
L. A. Harris, M. E. Gerstner and R. H. Wilson, *J. Electrochem. Soc.*, *124* (1977) 1511.
Y. Nakato, K. Abe and H. Tsubomura, *Ber. Bunsenges. Phys. Chem.*, *80* (1976) 1002.
Y. Nakato, S. Tonomura and H. Tsubomura, *Ber. Bunsenges. Phys. Chem.*, *80* (1976) 1289.

5 F.-T. Liou, C. Y. Yang and S. N. Levine, in W. L. Wallace, A. J. Nozik, S. K. Deb and R. H. Wilson (eds.), *Photoelectrochemistry: Fundamental Processes and Measurement Techniques*, Vol. 82-3, The Electrochemical Society, Princeton, 1982, p. 653.
H. Morisaki, H. Ono, H. Dohkoski and K. Yazawa, *Jpn. J. Appl. Phys.*, *19* (1980) L148.
M. Tomkiewicz and J. M. Woodall, *J. Electrochem. Soc.*, *124* (1977) 1437.
S. Wagner and J. Shay, *J. Appl. Phys. Lett.*, *31* (1977) 446.

6 K. C. Chang, A. Heller, B. Schwartz, S. Menezes and B. Miller, *Science*, *196* (1977) 1097.
A. B. Ellis, S. W. Kaiser and M. S. Wrighton, *J. Am. Chem. Soc.*, *98* (1976) 1635.

7 G. C. Calabrese, M.-S. Lin, J. Dresner and M. S. Wrighton, *J. Am. Chem. Soc.*, *104* (1982) 2412.
J. M. Bolts, A. B. Bocarsley, M. C. Palazzotto, E. G. Walton, N. S. Lewis and M. S. Wrighton, *J. Am. Chem. Soc.*, *101* (1979), 1378.
C. Cohen, G. Hodes and J. Manassen, *J. Electrochem. Soc.*, *125* (1978) 1623.

8 A. J. Frank and K. Honda, *J. Phys. Chem.*, *85* (1982) 1933.

9 A. J. Frank, in M. Grätzel (ed.), *Energy Resources through Photochemistry and Catalysis*, Academic Press, New York, 1983, p. 467.

10 A. J. Frank and K. Honda, *J. Electroanal. Chem.*, *150* (1983) 673.

11 K. Honda and A. J. Frank, *J. Phys. Chem.*, *88* (1984) 5577.

12 A. F. Diaz and J. I. Castillo, *J. Chem. Soc., Chem. Commun.*, (1980) 397.
K. K. Kanazawa, A. F. Diaz, W. D. Gill, P. M. Grant, G. B. Street, F. P. Gardini and J. F. Kwak, *Synth. Met.*, *1* (1979/80) 329.
K. K. Kanazawa, A. F. Diaz, R. H. Geiss, W. D. Gill, J. F. Kwak, J. A. Logan, J. F. Rabolt and G. B. Street, *J. Chem. Soc., Chem. Commun.*, (1979) 854.

13 G. Cooper, R. Noufi, A. J. Frank and A. J. Nozik, *Nature (London)*, *295* (1982) 578.

14 A. J. Frank, J. A. Turner and A. J. Nozik, in J. S. Connolly (ed.), *Abstr. 3rd Int. Conf. on Photochemistry Conversion Storage and Solar Energy, Golden, CO, 1980*, Solar Energy Research Institute, Golden, p. 299.

15 R. A. Bull, F.-R. F. Fan and A. J. Bard, *J. Electrochem. Soc.*, *129* (1982) 1009.

16 A. J. Frank, J. Cooper, R. Noufi, J. A. Turner and A. J. Nozik, in W. L. Wallace, A. J. Nozik, S. K. Deb and R. H. Wilson (eds.), *Photoelectrochemistry: Fundamental Processes and Measurement Techniques*, The Electrochemistry Society, Princeton, 1982, p. 248.

17 H. Gerischer, in B. O. Seraphin (ed.), *Topics in Applied Physics*, Vol. 31, Springer-Verlag, Berlin, 1979, p. 115.

18 A. J. Nozik, *Appl. Phys. Lett.*, *29* (1977) 567.

19 K. Kalyanasundaram, E. Borgarello and M. Grätzel, *Helv. Chim. Acta*, *64* (1981) 362.
K. Kalyanasundaram, E. Borgarello, D. Duonghong and M. Grätzel, *Angew. Chem.*, *93* (1981) 1012.

20 D. Meissner, R. Memming and B. Kastening, *Chem. Phys. Lett.*, *96* (1983) 34.

21 D. E. Aspnes and A. Heller, *J. Phys. Chem.*, *87* (1983) 4919.

22 A. Henglein, *J. Phys. Chem.*, *86* (1982) 2291.
A. Henglein and M. Gutierrez, *Ber. Bunsenges. Phys. Chem.*, *87* (1983) 852.

23 J. R. Harbour, R. Wolkow and M. L. Hair, *J. Phys. Chem.*, *85* (1981) 4026.
J. R. Harbour and M. L. Hair, *J. Phys. Chem.*, *82* (1978) 1978.

24 J. R. Darwent, *J. Chem. Soc., Faraday Trans. II*, *77* (1981) 1703.