

JOURNAL

OF THE AMERICAN CHEMICAL SOCIETY

Registered in U.S. Patent Office. © Copyright, 1980, by the American Chemical Society

VOLUME 102, NUMBER 16

JULY 30, 1980

Semiconductor Electrodes. 30. Spectral Sensitization of the Semiconductors n-TiO₂ and n-WO₃ with Metal Phthalocyanines

Alain Giraudeau, Fu-Ren F. Fan, and Allen J. Bard*

Contribution from the Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712. Received January 2, 1980

Abstract: Thin films (100–250 Å) of several phthalocyanines (MgPc, ZnPc, AlClPc, TiOPc, CoPc, FePc, H₂Pc) were investigated as sensitizers for photoelectrochemical processes at n-type TiO₂ and WO₃ single crystal electrodes in aqueous solution. The sensitized oxidation of several solution species (I⁻, Fe(CN)₆⁴⁻, hydroquinone, Fe(II)-EDTA) occurred with photocurrents proportional to light intensity and spectral responses characteristic of the metal phthalocyanine (MPc) films. At negative electrode potentials cathodic photocurrents for the reduction of benzoquinone, O₂, and Fe(III)-EDTA were observed, consistent with the p-type behavior of the phthalocyanines themselves. The photoelectrochemical behavior is rationalized from the energy levels of the semiconductors, solution couples, and MPc. The surface ionization potentials were found to yield better estimates of the phthalocyanine levels than the redox potentials of the MPc couples (measured in *N,N*-dimethylacetamide solutions).

Introduction

Photoactive dyes can be either adsorbed or covalently attached to semiconductor electrode surfaces to sensitize the electrode to visible-wavelength light and thus produce photocurrents or photovoltages at wavelengths longer than energies corresponding to the semiconductor band gap.¹⁻¹³ Such sensitization is also of interest because it provides information about the nature of charge transfer between excited states of surface species and electrodes. Sensitization by phthalocyanines is of interest for a number of reasons. Research on these materials has been very active recently,¹⁴ and much is known about the redox behavior of these species in solution,¹⁵ the surface ionization potentials in the solid

state,¹⁶ and their photoproperties.¹⁷ These compounds have many characteristics which suggest that they might be useful sensitizers for semiconductor electrodes: (1) they are chemically very stable; (2) they have highly absorbing chromophores within the solar spectrum; (3) a wide variety of metal phthalocyanines (MPc) have been prepared which allow a range of different compounds with different energy levels (i.e., redox potentials); (4) they often exhibit semiconducting behavior themselves.

Recently, we demonstrated that the behavior of the sensitized photocurrent by metal-free phthalocyanine (H₂Pc) thin films on several single-crystal n-type semiconductors correlated well with the relative positions of the energy levels of the semiconductors, H₂Pc, and the redox couples in solution.¹⁸ Both anodic and cathodic sensitized photocurrents could be observed for the same H₂Pc/semiconductor electrode depending upon the applied potential. The studies reported here concern the utilization of various metal phthalocyanines on n-WO₃ and n-TiO₂ single crystal electrodes. We show that the efficiencies of the sensitized photooxidation of several redox couples are strongly dependent on the potential for oxidation of MPc. These potentials for MPc

- (1) Gerischer, H.; Willig, F. *Top. Curr. Chem.* **1976**, *61*, 31.
- (2) Gerischer, H. *Photochem. Photobiol.* **1972**, *16*, 243, and references cited therein.
- (3) Spittler, M. T.; Calvin, M. *J. Chem. Phys.* **1977**, *66*, 4294.
- (4) Miyasaka, T.; Watanabe, T.; Fujishima, A.; Honda, K. *J. Am. Chem. Soc.* **1978**, *100*, 6657.
- (5) Kim, H.; Laitinen, H. A. *J. Electrochem. Soc.* **1975**, *122*, 53.
- (6) Hawn, D.; Armstrong, N. R. *J. Phys. Chem.* **1978**, *82*, 1288.
- (7) Fujihira, M.; Osa, T. *Nature (London)* **1976**, *264*, 349.
- (8) Meshitsuka, S.; Tamura, K. *J. Chem. Soc., Faraday Trans. 1* **1977**, *73*, 236.
- (9) Kommissarov, G. G. *Russ. J. Phys. Chem. (Engl. Transl.)* **1973**, *47*, 927.
- (10) Onoue, E.; Kokado, H.; Nakayama, T. *Trans. Electron. Dev. ED-19* **1972**, *471*.
- (11) Daltrozzo, E.; Tributsch, H. *Photogr. Sci. Eng.* **1975**, *19*, 308.
- (12) Memming, R. *Photochem. Photobiol.* **1972**, *16*, 325, and references cited therein. Gleria, M.; Memming, R. *Z. Phys. Chem. (Frankfurt am Main)* **1975**, *98*, 303.
- (13) Clark, W. D. K.; Sutin, N. *J. Am. Chem. Soc.* **1977**, *99*, 4676.
- (14) (a) Tachikawa, H.; Faulkner, L. R. *J. Am. Chem. Soc.* **1978**, *100*, 4399. (b) Fan, F.-R.; Faulkner, L. R. *J. Chem. Phys.* **1978**, *69*, 3334, 3341, and references cited therein. (c) Ghosh, A. K.; Morel, D. L.; Feng, T.; Shaw, R. F.; Rowe, C. A., Jr. *J. Appl. Phys.* **1974**, *45*, 230. (d) Harbour, J. R.; Hair, M. L. *Photochem. Photobiol.* **1978**, *28*, 721.

- (15) (a) Wolberg, A.; Manassen, J. *J. Am. Chem. Soc.* **1970**, *92*, 2982. (b) Clark, D. W.; Hush, N. S.; Woolsey, I. S. *Inorg. Chim. Acta* **1976**, *19*, 129. (c) Lever, A. B. P.; Wilshire, J. P. *Inorg. Chem.* **1978**, *17*, 1145. (d) Shepard, V. R., Jr.; Armstrong, N. R. *J. Phys. Chem.* **1979**, *83*, 1268.
- (16) (a) Kearns, D. R.; Calvin, M. *J. Chem. Phys.* **1961**, *34*, 2026. (b) Pope, M. *Ibid.* **1962**, *36*, 2810. (c) Vilesov, F. I.; Zagrubskii, A. A.; Garbuzov, D. Z. *Sov. Phys.-Solid State (Engl. Transl.)* **1964**, *5*, 1460.
- (17) (a) Papovic, Z. D.; Sharp, J. H. *J. Chem. Phys.* **1977**, *66*, 5076. (b) Meshitsuka, S.; Tamaru, K. *J. Chem. Soc., Faraday Trans. 1* **1977**, *73*, 760. (c) Minami, N.; Watanabe, T.; Fujishima, A.; Honda, K. *Ber. Bunsenges Phys. Chem.* **1979**, *83*, 476. (d) Hall, K. J.; Bonham, J. S.; Lyons, L. E. *Aust. J. Chem.* **1978**, *31*, 1661. (e) Fan, F.-R.; Faulkner, L. R. *J. Am. Chem. Soc.* **1979**, *101*, 4779.
- (18) Jaeger, C. D.; Fan, F.-R.; Bard, A. J. *J. Am. Chem. Soc.*, **1980**, *102*, 2592.

oxidation of thin films under illumination correlate better with the surface ionization potentials of thin films rather than with the redox potentials of these species in solution. The action spectra of the sensitized photocurrent, the current-potential (i - V) behavior, and the dependence of the sensitized photocurrent on light intensity are also described.

Experimental Section

Materials. All phthalocyanines except H₂Pc (Eastman Chemicals, Rochester, N.Y.) were supplied by Professor A. B. P. Lever and used without further purification. n-TiO₂ single crystals (donor density $\sim 10^{18}/\text{cm}^2$) were obtained from Fujii Titanium and n-WO₃ single crystals from Sandia Laboratory. The ohmic contact was made by plating In-Ga alloy on the rear side of each crystal which was polished first with fine sandpaper and then with 0.5- μm alumina on felt. A copper wire was then attached to the ohmic contact with conductive silver epoxy (Allied Product Corp., New Haven, Conn.) which was subsequently covered, along with the copper wire and the sides of crystals, leaving the front face exposed, with silicone rubber sealant (Dow Corning Corp., Midland, Mich.). The semiconductor material was then mounted onto an 8-in. long piece of 7-mm diameter glass tubing. Before use, n-TiO₂ electrodes were etched for 5–10 s in 50% HF–50% concentrated HNO₃–Br₂ (2 drops of Br₂ per 50 mL of etching solution) and then washed thoroughly with distilled water. n-WO₃ electrodes were etched for 5–10 s in concentrated H₂SO₄ and then rinsed with water. Reagent-grade *N,N*-dimethylacetamide (DMA) was obtained from Matheson Coleman and Bell (bp 164–166 °C) and purified further first by refluxing with CaH₂ under purified nitrogen for at least 6 h and then using the procedure and apparatus reported previously, method A.²¹ The alumina was allowed to settle, and the solution was decanted. The neutral alumina (ROC/RIC Chemicals Co., Belleville, N.J.) was dried before use under vacuum at 150 °C. Tetra-*n*-butylammonium perchlorate (TBAP), used as the supporting electrolyte in DMA, was polarographic grade (Southwestern Analytical Chemicals, Austin, Texas). The TBAP was recrystallized from ethyl acetate, dried in vacuo for 24 h, and then stored in a glovebox. All other chemicals were reagent grade and used without further purification.

The phthalocyanine thin films were prepared by vacuum evaporation as described in the previous paper.¹⁸ The thicknesses of the sublimed phthalocyanine thin films were estimated by spectrophotometric methods and ranged from 100 to 250 Å.

Apparatus. A conventional three-electrode, single-compartment cell was used for the electrochemical measurements in aqueous solutions. The electrochemical cell (volume ~ 25 mL) which contained the Pt disk or semiconductor working electrode was fitted with a flat Pyrex window for illumination of the semiconductor. Removable air-tight Teflon joints were used with the Pt disk or semiconductor electrode. A platinum coil was used as the counterelectrode and an aqueous saturated calomel electrode (SCE) as the reference electrode.

The cyclic voltammograms were obtained with a PAR (Princeton Applied Research 173 potentiostat, PAR 175 universal programmer, and PAR 179 current-to-voltage converter) and recorded on a Houston Instruments Model 2000 X-Y recorder (Austin, Texas). The action spectra and the sensitized i - V behavior were recorded with modulated irradiation and phase-sensitive detection techniques. A custom-built mechanical chopper and a PAR HR8 lock-in amplifier were used in these experiments. The light source was either an Oriel Corp. 450-W Xe lamp (Stamford, Conn.) or a 1.6-mW Spectra Physics Model 132 He-Ne laser. Experiments designed for specific wavelengths employed an Oriel 7240 grating monochromator with a 20-nm band-pass. A red filter (590-nm cut-on) was used with the xenon lamp. The radiant intensity was measured with an E G & G Model 550 radiometer/photometer (Salem, Mass.). All photocurrent-action spectra have been normalized against the photon flux of the lamp-monochromator. If not otherwise mentioned, all experiments were carried out with the solution deaerated and maintained under purified nitrogen and the pH buffered at 6.9 with 0.25 M phosphate buffer.

The cyclic voltammetric measurements in DMA were carried out in a VAC HE 43-2 Dri-Lab with M0 40-1 Dri-Train glovebox (Vacuum Atmospheres Corp., Hawthorne, Calif.). The working electrode was a platinum disk and the counterelectrode was a platinum coil. A silver electrode was used as a quasi-reference electrode whose potential was in turn referenced to the first reduction potential of *p*-benzoquinone (–0.52

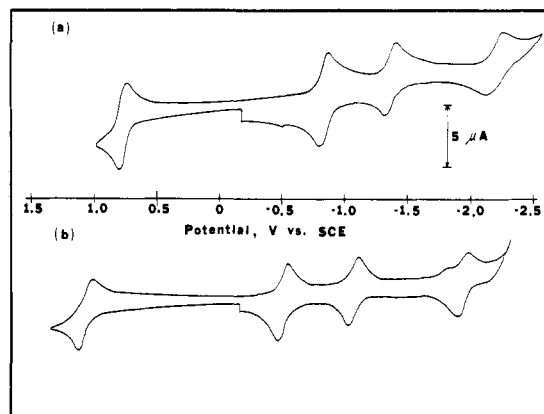


Figure 1. Cyclic voltammograms of ~ 0.4 mM phthalocyanines in 0.1 M TBAP-DMA at Pt electrode; scan rate 50 mV/s. (a) ZnPc; (b) AlPcCl.

Table I. Potentials for the First Oxidation and Reduction of the Metal Phthalocyanines^a

phthalocyanine	potential for first oxidn, V vs. SCE	potential for first redn, V vs. SCE
AlPcCl	1.15	–0.50 –0.53 ^b
H ₂ Pc	1.10 ^c	–0.66 ^b
CuPc	0.98 ^c	–0.84 ^b
CoPc	0.80 0.77 ^c	–0.20 –0.37 ^b
ZnPc	0.78 0.68 ^c	–0.80 –0.89 ^b
MgPc	0.70	–0.95 –0.91 ^b
FePc	0.38 ^d	

^a The potential taken here is the average of the two peak potentials since the cyclic voltammograms are fairly reversible; $\sim 5 \times 10^{-4}$ M solutions of MPc in 0.1 M tetra-*n*-butylammonium perchlorate/*N,N*-dimethylacetamide (DMA). ^b From ref 15b; in *N,N*-dimethylformamide. ^c From ref 15a; in 0.1 M tetra-*n*-butylammonium perchlorate/1-chloronaphthalene. ^d From ref 15c; in tetraethylammonium perchlorate/DMA.

V vs. aqueous SCE in DMA). The concentrations of phthalocyanines were about $3\text{--}5 \times 10^{-4}$ M.

The absorption spectra of phthalocyanine solutions in DMA or the phthalocyanine thin film on microscope slides were carried out on a Cary Model 14 spectrophotometer.

Results

Voltammetric Data in DMA. Typical cyclic voltammograms of ZnPc and AlPcCl at a Pt electrode are shown in Figure 1. ZnPc shows three well-defined reduction-reoxidation peaks in the potential range studied. The peak current ratio of the cathodic wave to the reverse anodic wave is one. The peak potential separation is ~ 60 mV. Moreover, $i_{pc}/Av^{1/2}C$ (where i_{pc} is the peak cathodic current, A is the electrode area, C is the MPc concentration, and v is the scan rate) is $\sim 540 \mu\text{A s}^{1/2} \text{cm}^{-2} \text{mM}^{-1} \text{V}^{-1/2}$. These cyclic voltammetric parameters show that the first two reduction waves are reversible, one-electron processes. These results imply that monoanions and dianions of ZnPc are stable on this time scale ($v = 50$ mV/s) in DMA. The first oxidation wave is also a reversible, one-electron process. AlPcCl shows two reversible, one-electron reduction waves. The third reduction, by its wave shape, apparently involves some adsorption process. The oxidation of AlPcCl occurs at a fairly positive potential, ~ 1.20 V vs. SCE. The potentials for the first oxidation and first reduction for several phthalocyanines in DMA are given in Table I. These potentials represent the average of the anodic and the cathodic peak potentials. Since the cyclic voltammograms are fairly reversible, these values are probably close to the formal potentials of the half-reactions. The agreement of our data with previously reported data¹⁵ is fairly good.

(19) Fan, F.-R. F.; Reichman, B.; Bard, A. J. *J. Am. Chem. Soc.*, **1980**, *102*, 1488.

(20) (a) Royes, R. M. *J. Am. Chem. Soc.* **1962**, *84*, 513. (b) Lohmann, F. Z. *Naturforsch. A* **1967**, *22*, 843. (c) Gomer, R.; Tryson, G. *J. Chem. Phys.* **1977**, *66*, 4413.

(21) Faulkner, L. R.; Bard, A. J. *J. Am. Chem. Soc.* **1968**, *90*, 6284.

Table II. Summary of the Behavior of the Metal Phthalocyanines on *n*-WO₃ and *n*-TiO₂^a

WO ₃							TiO ₂					
AlPc ⁺	TiOPc	H ₂ Pc	CoPc	ZnPc	MgPc	FePc	H ₂ Pc	AlPc	ZnPc	MgPc		
I	I	I	I	I	I	I	I	I	I	I	H ₂ O	↑ oxidn
I	I	I									Cl ⁻	
I	I	I									Br ⁻	
II	II	III	I	II	I	I	III	II		I	I ⁻	↑ oxidn
III	III	III	III	III	II	II	III	III		II	Fe[CN] ₆ ⁴⁻	
III	III	III	III	III	II	III	III			III	HQ	
				III	III						Fe-EDTA ²⁻	↓ redn
redn	redn	redn	no redn	redn	redn	*redn	redn		redn	redn	BQ	
*redn	redn	redn		redn	redn	*redn	redn		redn	redn	Fe-EDTA ⁻	
*	redn			redn	redn	*	redn		redn	redn	O ₂	

^a I, type 1 anodic photosensitization behavior (no oxidation of solution species); II, type 2 behavior (partial oxidation of solution species); III, type 3 behavior (rapid oxidation of solution species). See text for the meanings of these three types of behavior. An asterisk indicates that MPC film became detached from electrode.

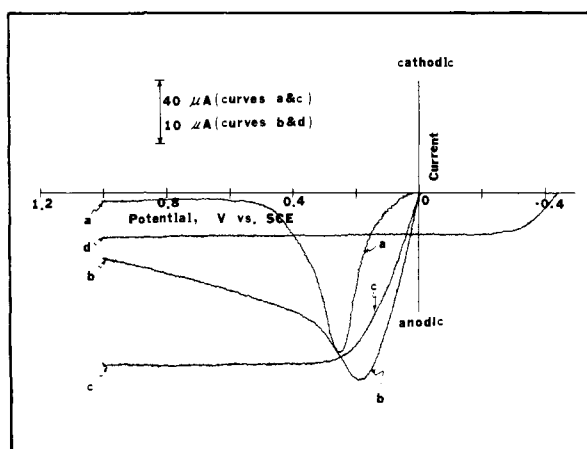


Figure 2. Current-potential curves with a 0.50 M Na₂SO₄, 0.25 M phosphate buffer (pH ~6.9), illuminated with a 1.6-mW He-Ne laser (632.8 nm), phase-sensitive technique being used to record the *i*-*V* curves. (a) WO₃-TiOPc electrode without reducing agents other than water; (b) WO₃-ZnPc electrode with 50 mM I⁻; (c) WO₃-TiOPc electrode with 50 mM K₄Fe(CN)₆; (d) TiO₂-AlPcCl electrode with 50 mM K₄Fe(CN)₆.

Current-Potential Behavior of Phthalocyanine-Coated Semiconductor Electrodes. Sensitized Photooxidation. The anodic photocurrent-potential curves for the phthalocyanine-coated *n*-WO₃ electrodes during illumination with light of energy less than the band gap (*E_g*) of *n*-WO₃ (i.e., λ > 590 nm) can be classified into three categories, depending on the phthalocyanine used and the redox species present in the solution. In the first category, no sensitized photooxidation of the solution species is observed. This behavior was found with H₂O, Cl⁻, and Br⁻ in solution with almost all of the phthalocyanines used in this study. A typical photocurrent-potential curve, shown in Figure 2a, illustrates the behavior of a *n*-WO₃/TiOPc electrode. An anodic photocurrent, probably due to the photooxidation of the MPC itself, starts at potentials ~0 V vs. SCE. This anodic onset photopotential, *V_{on}*, is close to the flat-band potential (*V_{fb}*), ~0 V vs. SCE, of *n*-WO₃ electrodes and is nearly independent of the phthalocyanines used in this study. The sensitized anodic photocurrent reaches a maximum on scanning toward positive potentials at around 0.10–0.25 V vs. SCE and then decreases to essentially zero at more positive potentials. The second type of photovoltammetric behavior is illustrated by Figure 2b. The sensitized photooxidation of I⁻ at *n*-WO₃/ZnPc and those of hydroquinone and ferrocyanide by *n*-WO₃/MgPc belong to this category. Different from type I behavior, type II curves have a significant residual sensitized photocurrent at potentials positive of the peak potential. In the third type of sensitized photooxidation, as shown in Figure 2c, the photocurrent attained a limiting (saturated) level when the concentration of reducing agent (i.e., supersensitizer) was sufficiently high. For this case, the anodic onset photopotentials were also close to the *V_{fb}* values of *n*-WO₃ electrodes. As summarized in

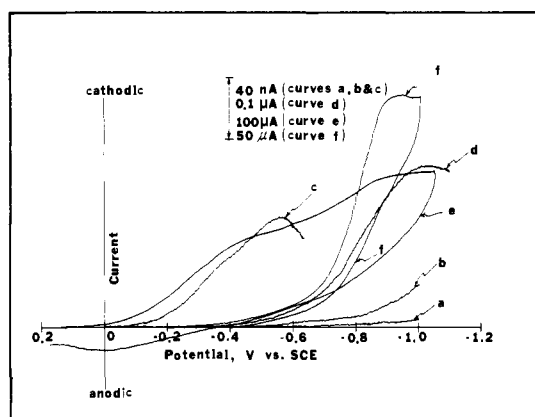


Figure 3. Voltammetric curves with a 0.50 M Na₂SO₄ containing phosphate buffer (pH ~6.9), if not otherwise mentioned. A 1.6-mW He-Ne laser was used as the light source in photoeffect measurement. Phase-sensitive detection technique was used to record the photocurrent-potential curves. (a) WO₃-ZnPc electrode with no added reducing agents; (b) as (a) for TiO₂-ZnPc electrode; (c) WO₃-ZnPc electrode with ~20 mM *p*-benzoquinone; (d) TiO₂-ZnPc electrode with ~20 mM *p*-benzoquinone; (e) cyclic voltammograms on WO₃-ZnPc electrode in ~20 mM *p*-benzoquinone in the dark; (f) cyclic voltammograms on TiO₂-ZnPc electrode in ~20 mM *p*-benzoquinone in the dark.

in Table II, sensitized photooxidation of electroactive species with redox potentials more negative than that of I⁻ by most phthalocyanines used in this study (except MgPc) falls into this category.

The results, summarized in Table II, show that similar sensitized photooxidation behavior occurs on phthalocyanines coated on *n*-TiO₂ electrodes. However, the anodic onset photopotentials were shifted to more negative potentials compared to *n*-WO₃ systems. As shown in Figure 2d, *V_{on}* for MPC/*n*-TiO₂ electrodes at pH 7 was ~-0.45 V vs. SCE, which is close to *V_{fb}* of *n*-TiO₂.

Sensitized Photoreduction. As discussed in previous reports^{14,18} the phthalocyanines themselves are *p*-type materials and can thus produce cathodic photocurrents at more negative potentials. The cathodic photocurrent-potential curves for the phthalocyanine-coated *n*-WO₃ or *n*-TiO₂ electrodes at potentials negative of *V_{on}* show that the cathodic photocurrent is strongly affected by the presence of oxidizing agents in the solution (e.g., *p*-benzoquinone, Fe(III)-EDTA, O₂, etc.). Except for AlPcCl and CoPc, where the thin films broke easily during cathodization, most phthalocyanine-coated *n*-WO₃ and *n*-TiO₂ electrodes showed higher cathodic photocurrent than anodic sensitized ones. Several examples are shown in Figure 3. With no added oxidizing agents only small cathodic photocurrents were observed at potentials negative of ~0 V vs. SCE on *n*-WO₃/ZnPc electrodes (curve a) and of ~-0.45 V vs. SCE on *n*-TiO₂/ZnPc electrode (curve b). The addition of *p*-benzoquinone (or Fe(III)-EDTA, or O₂) into the solution shifted *V_{on}* to slightly more positive potentials and enhanced substantially the cathodic photocurrent. The cathodic photocurrent showed a maximum around the cathodic peak potential, *V_{pc}*, in the dark cyclic voltammogram. (See curves c and

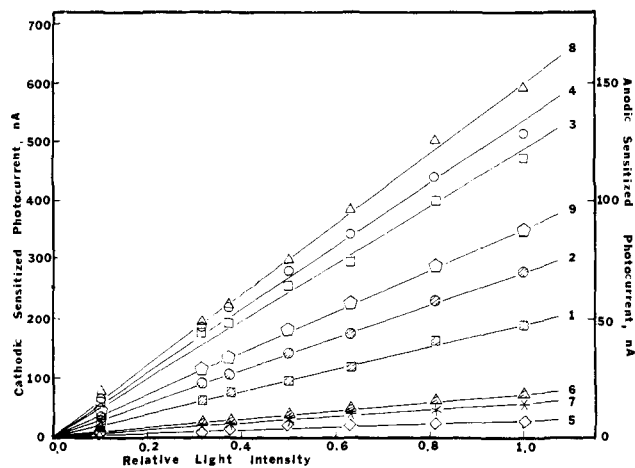


Figure 4. The light intensity dependence of the sensitized photocurrents; 0.50 M Na₂SO₄ and 0.25 M phosphate buffer (pH ~6.9), if not otherwise mentioned; 1.6-mW He-Ne laser (632.8 nm) as the light source. Curves 1-7: anodic sensitized photocurrent. Curves 8 and 9: cathodic sensitized photocurrent. (1) WO₃-ZnPc; 50 mM K₄Fe(CN)₆; biased at 0.6 V vs. SCE. (2) WO₃-ZnPc; 50 mM Fe(II)-EDTA; biased at 0.6 V vs. SCE; no phosphate buffer, pH ~5. (3) WO₃-TiOPc; 50 mM NaI; biased at 0.6 V vs. SCE. (4) WO₃-TiOPc; 50 mM K₄Fe(CN)₆; biased at 0.6 V vs. SCE. (5) WO₃-CoPc; 50 mM *p*-hydroquinone; biased at 0.6 V vs. SCE. (6) WO₃-H₂Pc; 50 mM NaI; biased at 0.6 V vs. SCE. (7) WO₃-H₂Pc; 50 mM K₄Fe(CN)₆; biased at 0.6 V vs. SCE. (8) WO₃-TiOPc; 50 mM Fe(III)-EDTA; biased at -0.7 V vs. SCE; no phosphate buffer, pH ~5. (9) WO₃-H₂Pc; 50 mM Fe(III)-EDTA; biased at -0.7 V vs. SCE; no phosphate buffer, pH ~5.

Table III. Quantum Efficiency of Sensitized Anodic and Cathodic Photocurrents^a

system	ϕ_a^b , %	ϕ_c^c , %	ϕ_a^d , %	ϕ_c^e , %
n-WO ₃ -ZnPc/ Fe(CN) ₆ ⁴⁻	6.0×10^{-3}		4.0×10^{-2}	
n-WO ₃ -ZnPc/ Fe(II)-EDTA ^f	8.8×10^{-3}		5.8×10^{-2}	
n-WO ₃ -TiOPc/I ⁻	1.5×10^{-2}		1.0×10^{-1}	
n-WO ₃ -TiOPc/ Fe(CN) ₆ ⁴⁻	1.6×10^{-2}		1.1×10^{-1}	
n-WO ₃ -CoPc/ <i>p</i> -hydroquinone	8.7×10^{-4}		6.0×10^{-3}	
n-WO ₃ -H ₂ Pc/I ⁻	2.3×10^{-3}		1.5×10^{-2}	
n-WO ₃ -H ₂ Pc/ Fe(CN) ₆ ⁴⁻	1.9×10^{-3}		1.3×10^{-3}	
n-WO ₃ -TiOPc/ Fe(III)-EDTA ^f		7.5×10^{-2}		5.0×10^{-1}
n-WO ₃ -H ₂ Pc/ Fe(III)-EDTA ^f		4.4×10^{-2}		2.9×10^{-1}

^a 0.50 M Na₂SO₄ and 0.25 M phosphate buffer (pH ~6.9) as the supporting electrolyte, unless otherwise noted; 1.6-mW He-Ne laser (632.8 nm) as the light source. ^b The incident quantum efficiency for the anodic sensitized photocurrent. ^c The incident quantum efficiency for the cathodic photocurrent. ^d The quantum efficiency based on the adsorbed photons by phthalocyanine thin films for the anodic sensitized photocurrent. ^e The quantum efficiency based on the adsorbed photons for the cathodic photocurrent. ^f No phosphate buffer was used; pH ~5. ^g This quantum efficiency was normalized to the same absorption (OD of thin film = 0.15), assuming that ϕ was not changed by small variations of the film thickness.

d.) The decrease in the cathodic photocurrent at potentials negative of V_{pc} during scanning can probably be attributed to mass transfer effects (i.e., the current being limited by diffusion of the oxidant to the electrode). The extent of this current fall-off was diminished and the photocurrent was enhanced by stirring the solution.

Dependence of Sensitized Photocurrent on Light Intensity. The dependence of the sensitized photocurrent for several redox systems to light intensity on phthalocyanine-coated n-WO₃ electrodes is shown in Figure 4. Both cathodic and anodic sensitized photocurrent showed a linear dependence with light intensity in most

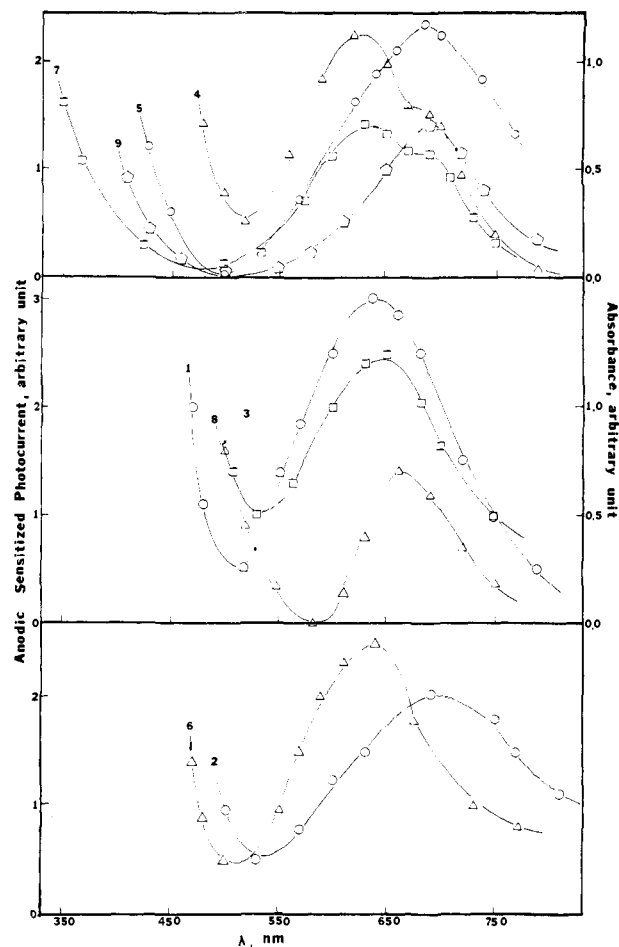


Figure 5. Action spectra of anodic sensitized photocurrents (curves 1-6) and absorption spectra of phthalocyanine thin films (7-9). A 430-nm cut-on filter was used to cut off higher order harmonics. (1) WO₃-ZnPc; 0.50 M Na₂SO₄, 0.25 M phosphate buffer (pH ~6.9), and 50 mM K₄Fe(CN)₆; biased at 0.6 V vs. SCE. (2) WO₃-TiOPc; 0.50 M Na₂SO₄, 0.25 M phosphate buffer (pH ~6.9), and 50 mM NaI; biased at 0.6 V vs. SCE. (3) WO₃-CoPc; 0.50 M Na₂SO₄, 0.25 M phosphate buffer (pH ~6.9), and 50 mM *p*-hydroquinone; biased at 0.6 V vs. SCE. (4) WO₃-H₂Pc; 0.50 M Na₂SO₄, 0.25 M phosphate buffer (pH ~6.9), and 50 mM *p*-hydroquinone; biased at 0.6 V vs. SCE. (5) WO₃-MgPc; 0.50 M Na₂SO₄ and 50 mM Fe(II)-EDTA (pH ~5); biased at 0.6 V vs. SCE. (6) WO₃-AlPcCl; 0.50 M Na₂SO₄, 0.25 M phosphate buffer (pH ~6.9), and 50 mM K₄Fe(CN)₆; biased at 0.6 V vs. SCE. (7) H₂Pc. (8) CoPc. (9) MgPc.

cases, at least up to the highest proton flux employed in the present study. These experiments were conducted with a He-Ne laser (1.6 mW, 632.8 nm) and neutral density filter to vary the light intensity. Based upon the slopes of the straight lines shown in Figure 4, the incident quantum efficiency, ϕ' , was calculated; these are summarized in Table III. To allow comparisons, the ϕ' values are normalized to the same absorbance (0.15), which is close to the absorbances of most of the phthalocyanine thin films studied here (~200 Å). ϕ' is only slightly dependent on the solution redox couples for a given phthalocyanine, if type III sensitization behavior is fulfilled (compare curves 3 and 4 or curves 6 and 7). This is reasonable, since type III sensitized photocurrents at constant light intensity are essentially controlled by the electrode itself. It is interesting to note that different phthalocyanines show substantially different ϕ' values for a given redox couple (compare curves 1, 4, and 7). TiOPc showed the highest efficiencies for both anodic and cathodic sensitization.

Sensitized Photocurrent-Wavelength Response. The anodic and cathodic sensitized photocurrent action spectra on phthalocyanine-coated n-WO₃ electrodes are shown in Figures 5 and 6, respectively. The sensitized photocurrents are corrected for the number of incident photons (in arbitrary units). Generally, as shown in these figures, both the anodic and cathodic photosen-

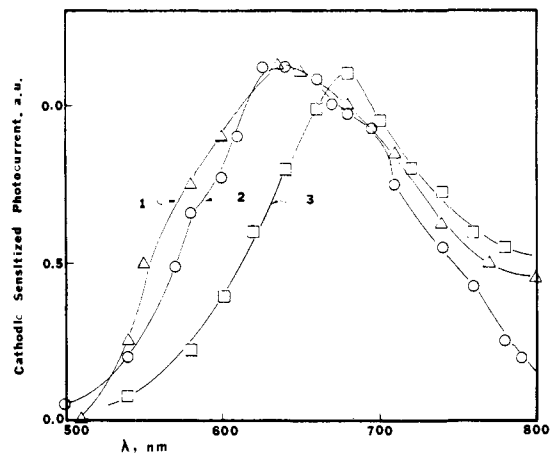


Figure 6. Action spectra of cathodic sensitized photocurrents. A 430-nm cut-on filter was used to remove higher order harmonics. (1) WO₃-ZnPc; 0.50 M Na₂SO₄, 0.25 M phosphate buffer (pH ~6.9), and 50 mM *p*-benzoquinone; biased at -0.7 V vs. SCE. (2) WO₃-H₂Pc; same solution as in (1); biased at -0.7 V vs. SCE. (3) WO₃-MgPc; same solution as in (1); biased at -0.7 V vs. SCE.

sitized current action spectra were close to the absorption spectra of the phthalocyanine thin films. The positions of the peaks of the sensitized photocurrents vary significantly with different phthalocyanines, although their shapes, similar to those of the absorption spectra, are essentially structureless. Similar results were obtained for phthalocyanine-coated *n*-TiO₂ electrodes.

Discussion

The interpretation of dye-sensitized photocurrents at semiconductor electrodes is usually based on diagrams showing the energy levels of the semiconductors, the solution redox couples, and the sensitizing dyes, as shown in Figure 7.¹ The energy levels are frequently presented on a scale of electrode potentials (vs. NHE), so that the redox couples are shown at their standard (or formal) potentials, V° , and the positions of the semiconductor bands are estimated from the flat-band potentials. A question arises, however, on the appropriate method of representing the energy levels of the thin films of the sensitizer (i.e., MPc) on the electrode surface. If these are considered as equivalent to the solution species, then these can be estimated from the cyclic voltammetric potentials for the first oxidation and reduction waves in an appropriate solvent as given in Table I. Transposition of these values to aqueous solutions involves an estimation of the liquid junction potential; such values are shown on the right-hand side of Figure 7. If the dye layers are closer to the bulk solids, then these energy levels are more appropriately estimated from the ionization potential of the solid and the spectral properties. Most of the ionization potentials reported so far for the phthalocyanines are actually surface ionization potentials, I_s , which perhaps are more useful than bulk ionization potentials in determining the appropriate energy level for rationalizing the charge-transfer behavior at the semiconductor/phthalocyanine or the phthalocyanine/solution interface. The surface ionization potentials of phthalocyanines have been studied by several techniques.^{14b,16} The I_s values determined from these methods show some scatter but usually agreed with each other within ~0.2 V. The average I_s values and the absorption spectra of the phthalocyanines were used to estimate the energy levels shown in Figure 7. Placement of these I_s values on the electrode potential scale required the usual assumption²⁰ that 0 V vs. NHE is equivalent to -4.5 to -4.7 eV vs. vacuum. In the series of phthalocyanines whose first oxidation potentials involve ligand oxidation^{15a} and which contain divalent central metal ions, or their equivalents (i.e., H₂Pc, ZnPc, MgPc, and CuPc), the difference between the potential for the first oxidation and I_s is ~+0.7 (±0.1) V. This relation might be useful in estimating I_s from the first oxidation potentials, if the above criteria are fulfilled and similar solvents are used. A change in the central metal ion from divalent to trivalent (such as Al³⁺) or tetravalent (such as Ti⁴⁺) results in

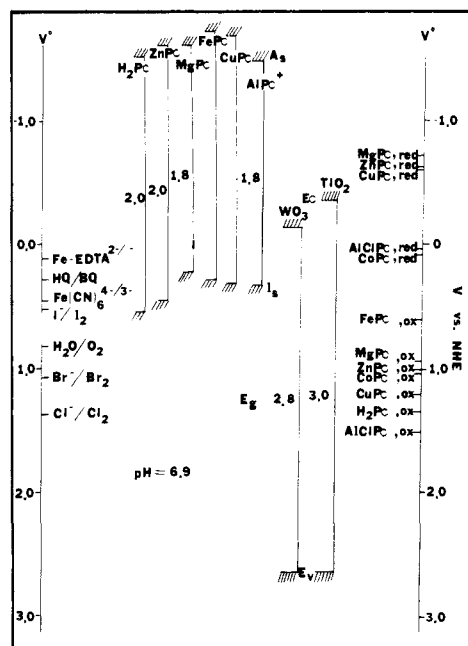


Figure 7. Energy levels of oxide semiconductors, phthalocyanine thin films, redox couples (pH ~6.9), and phthalocyanines in DMA (V vs. NHE). V° = standard potentials; A_s = surface electron affinity of phthalocyanine thin film; I_s = surface ionization potential of phthalocyanine thin film; E_c = conduction band edge of oxide semiconductor; E_g = band gap of oxide semiconductor; E_v = valence band edge of oxide semiconductor.

a shift in the first ligand oxidation potential to more positive values. This effect is well known in the oxidation of metalloporphyrins.^{15a} Note, however, that the surface ionization potentials are relatively insensitive to the nature and valency of the central metal ions. In fact the surface ionization potentials shown in Figure 7 suggest that potentials for oxidation of the different phthalocyanine thin films are nearly the same. This insensitivity of I_s to the central metal ion is also reflected in the similarity of the anodic photosensitization behavior of the different MPc compounds shown in Table II and discussed below.

Anodic Sensitized Photocurrent. The three types of anodic photosensitization behavior shown in Figure 2 and summarized in Table II can be satisfactorily explained in terms of the relative positions of the energy levels of phthalocyanine thin films, the energy bands of oxide semiconductors, and the redox potentials of the electroactive species in the solution. Consider first the energy levels of phthalocyanine thin films in terms of I_s and the surface electron affinities, A_s , which are calculated from I_s and the energy gaps of phthalocyanines. Energetically, as shown in Figure 7, all phthalocyanines studied here are able to inject electrons through photoexcitation into the conduction band of either an *n*-WO₃ or *n*-TiO₂ electrode. The differences in the observed photosensitization behavior can be attributed to differences in the oxidation rates of the reducing species by the photogenerated holes at the surface of phthalocyanine thin films. Thermodynamically, a hole at a potential I_s can readily oxidize a species with a V° more negative than I_s and will not oxidize a species with V° much more positive than I_s . Intermediate behavior and perhaps slower electron transfer will be observed if $V^\circ \approx I_s$. These criteria can be used to rationalize the observed anodic photosensitization behavior as follows. The oxidations of H₂O, Cl⁻, and Br⁻ are energetically unfavorable for all of the phthalocyanines studied. Even H₂Pc, which has the most positive I_s values, still cannot generate holes at a sufficiently positive potential to oxidize these species; thus type I behavior is found. The oxidations of *p*-hydroquinone and Fe(II)-EDTA are energetically favorable for all of the phthalocyanines studied, yielding type III behavior. Between these two extremes are the photooxidations of Fe(CN)₆⁴⁻ and I⁻. The effects summarized in Table II follow these energy criteria quite well.

On the other hand, predictions based on the redox potentials of the phthalocyanines determined in DMA do not work very well. For example, AlClPc, TiOPc, and H₂Pc would be expected to sensitize the oxidation of Cl⁻, Br⁻, and H₂O based on the MPc/MPc⁺ potential but they did not.

Cathodic Photocurrent. A mechanism for the anodic and cathodic photocurrents on H₂Pc-coated semiconductor electrodes has been proposed in a previous paper,¹⁸ and will not be repeated here. The reduction of an oxidizing species in the solution by photogenerated electrons occurs only when their potentials are more negative than the V° of the redox species and the potential of the electrode is sufficiently negative to force these electrons to the solution interface. The surface electron affinities of all phthalocyanines used in this study are negative enough to supply electrons via illumination to reduce the oxidizing agents listed in Table II (Fe(III)-EDTA, BQ, O₂). Nonselective reduction, as expected, was observed. Note, however, that the energetically possible reduction of protons to H₂ did not take place, probably because the overall reaction is slow. Most p-type semiconductors, e.g., p-GaAs, are not good H₂-generation electrodes.¹⁹

Action Spectra and Dependence of the Sensitized Photocurrent on Light Intensity. The linear dependence of the sensitized photocurrent on the incident light intensity, I_0 , implies that the sensitized photocurrent is proportional to the total rate of production of charge carriers G . The expected spectral shapes can be estimated from absorption data. The rate of carrier generation as a function of distance, x , from the illuminated surface is proportional to $\alpha \exp(-\alpha x)$, where α is the absorption coefficient of the phthalocyanine thin film. Since the film thickness, 100-250 Å, is of the order of the width of the space charge layer of the phthalocyanine thin film,^{14b,c} it is assumed that the space charge layer in phthalocyanine extends the whole film thickness. The total rate of carrier production, G , is thus given by

$$G = \phi \int_0^d I_0 \alpha \exp(-\alpha x) dx = \phi I_0 [1 - \exp(-\alpha d)] \quad (1)$$

where d is the film thickness and ϕ is the quantum efficiency of

carrier generation. Because the film thickness is much smaller than the optical penetration depth (for example, even at maximal absorption, only ~15% of incident light was absorbed by the film), eq 1 can be reduced to

$$G \approx \phi I_0 \alpha d = \phi I_0 A \quad (2)$$

or

$$G/I_0 \approx \Phi A \quad (3)$$

where A is the absorbance of thin phthalocyanine films. Thus, if G is normalized to the same incident light intensity at every wavelength, the action spectra of the sensitized photocurrent will be expected to correspond to the absorption spectra. This is observed, at least for the general shapes, for both anodic and cathodic photocurrents.

Conclusion

The foregoing discussion shows that the surface ionization potentials, I_s , of the phthalocyanine thin films rather than the oxidation potentials of phthalocyanines in solution determine the actual oxidizing power of the photoexcited phthalocyanine molecules. Thus, attempts at using different central metal ions or changes in valency to shift I_s to more positive values for the sensitized photooxidation of H₂O, Br⁻, and Cl⁻ seem rather unpromising; the I_s values are rather insensitive to these parameters.

An alternative approach is to modify the phthalocyanine ring by electron-withdrawing substituents and this is now under investigation. As found in previous studies with phthalocyanine materials^{14,18} the quantum efficiencies for conversion of absorbed radiation to external current flow are rather low, probably because of inefficient production or rapid recombination of the charge carriers. The utilization of MPc sensitization in practical devices will require significant improvements in these quantum efficiencies.

Acknowledgments. The support of this research, which is a joint project with Professor A. B. P. Lever of York University, by the Office of Naval Research is gratefully acknowledged.

Semiconductor Electrodes. 31. Photoelectrochemistry and Photovoltaic Systems with n- and p-Type WSe₂ in Aqueous Solution

Fu-Ren F. Fan, Henry S. White, Bob L. Wheeler, and Allen J. Bard*

Contribution from the Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712. Received January 2, 1980

Abstract: The photoelectrochemical (PEC) behavior of n- and p-type WSe₂ single crystal electrodes in aqueous solutions containing a number of redox couples (Br₂/Br⁻, Fe³⁺/Fe²⁺, I₂/I⁻, Fe(CN)₆³⁻/Fe(CN)₆⁴⁻, and MV²⁺/MV⁺, where MV is methylviologen) was investigated. The results are consistent with a model of the interface where ideal behavior is approached with some couples but recombination effects are important with others. The characteristics of several PEC cells are described. The n-WSe₂/I₃⁻ (0.025 M), I⁻ (1.0 M)/Pt cell showed a 0.71-V open circuit voltage, 65 mA/cm² short circuit current, 0.46 fill factor, and ~14% power efficiency under 150 mW/cm² red light irradiation. A rechargeable PEC cell based on the p-WSe₂/MV²⁺, I⁻/n-WSe₂ system was constructed. Photoproduction of H₂ and I₂ with such a cell is also described.

Introduction

The application of semiconductor electrodes to the construction of photoelectrochemical (PEC) photovoltaic and electrophotovoltaic cells has been reviewed recently.¹ In addition to fun-

damental studies of the semiconductor/solution interface, investigations of such electrodes are concerned with the construction of efficient systems for the utilization of solar energy to produce electricity or chemical species. The practical application of such devices depends upon the discovery of inexpensive and abundant materials with an energy gap which matches the solar spectrum and which are capable of stable operation in solution over an extended period. This has led to the investigation of a number

(1) (a) Bard, A. J. *J. Photochem.* 1979, 10, 59. (b) *Science*, 1980, 207, 139. (c) Wrighton, M. S. *Acc. Chem. Res.* 1979, 12, 303. (d) Nozik, A. J. *Annu. Rev. Phys. Chem.* 1978, 29, 189.