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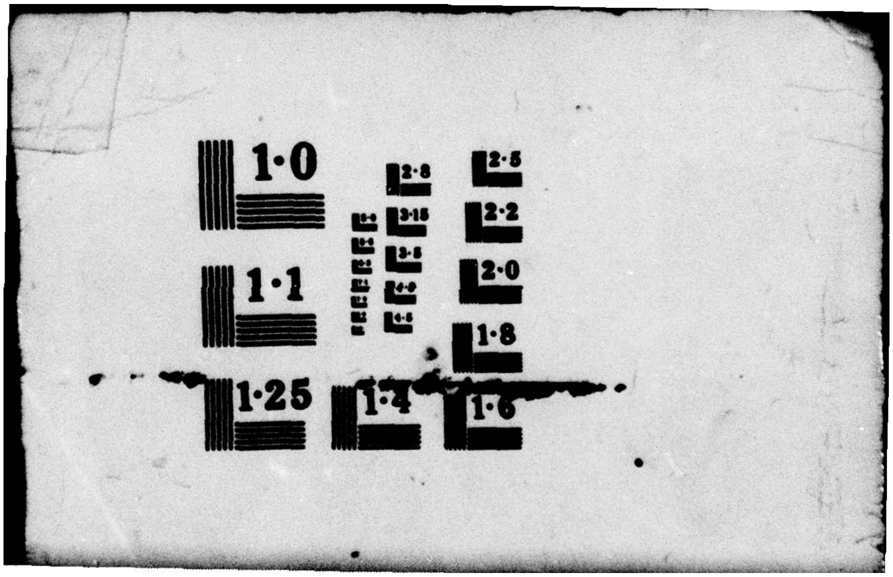
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Task No. NR 051-693

(9) TECHNICAL REPORT [redacted] 1 Sep 78-31 Aug 79

(6)

Spectral Sensitization of the Heterogeneous Photocatalytic Oxidation of Hydroquinone in Aqueous Solutions at Phthalocyanine-Coated TiO_2 Powders

by

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(15) N00014-78-C-059

Prepared for Publication

in the

Journal of the American Chemical Society

(14) TR-1

The University of Texas at Austin
Department of Chemistry
Austin, Texas 78712

(11) 1 Augu[redacted]1979

(12) 15p.

JOB

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

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1. REPORT NUMBER 1	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) SPECTRAL SENSITIZATION OF THE HETEROGENEOUS PHOTOCATALYTIC OXIDATION OF HYDROQUINONE IN AQUEOUS SOLUTIONS AT PHTHALOCYANINE-COATED TiO_2 POWDERS		5. TYPE OF REPORT & PERIOD COVERED 1 Sept. 1978 to 31 Aug. 1979 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Fu-Ren F. Fan and Allen J. Bard		8. CONTRACT OR GRANT NUMBER(s) N00014-78-C-0592
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry University of Texas at Austin Austin, TX 78712		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research 800 N. Quincy Arlington, VA 22217		12. REPORT DATE August 1, 1979 13. NUMBER OF PAGES 16
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

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19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

phthalocyanine
photoelectrochemistry
heterogeneous photocatalysis

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

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Spectral Sensitization of the Heterogeneous Photocatalytic Oxidation of Hydroquinone in Aqueous Solutions at Phthalocyanine-Coated TiO_2 Powders

(ABSTRACT)

The photocatalyzed reaction of hydroquinone with oxygen at TiO_2 (anatase) powders coated with metal-free or magnesium phthalocyanine under irradiation with light of energy less than the TiO_2 band gap is described. The behavior at the powders is correlated with current-potential curves at single crystal n-type TiO_2 electrodes and an energy level scheme for the reaction is proposed.

(End of Abstract)

Spectral Sensitization of the Heterogeneous Photocatalytic Oxidation of Hydroquinone in Aqueous Solutions at Phthalocyanine-Coated TiO_2 Powders

Sir:

Recent investigations have described the application of the principles of semiconductor electrodes to the design of large surface area powders that serve as photocatalysts for reactions of fundamental and practical interest.[1] These photocatalysts were generally materials with wide band gaps and thus they only absorb a small fraction of the available sunlight. However 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 longer wavelengths.[2-14] We were intrigued by the possibility that dye-coated semiconductor powders could be employed as useful sensitized heterogeneous photocatalysts with an improved response to visible light. The phthalocyanines appear most appropriate for this study because (1) they are chemically very stable, (2) they have highly absorbing chromophores within the solar spectrum, (3) they have moderately high electrical conductivity so that reasonably thick films with good optical absorption can be prepared, and (4) their redox potentials can be varied by changes in the central metal. To our knowledge spectral sensitization of semiconductor powders has not yet been demonstrated, although Uchida, et. al.,[15] have shown that the photocatalytic activities for the oxidation of isopropanol on phthalocyanine-covered ZnO correlated with the oxidation potentials of the phthalocyanine.

We report here the photocatalyzed oxidation of hydroquinone by oxygen in the presence of phthalocyanine-coated TiO_2 powder in the anatase form. The phthalocyanine-coated TiO_2 catalysts were prepared as follows. The phthalocyanines, either metal-free (H_2Pc) or magnesium phthalocyanine (MgPc), were dissolved in N,N'-dimethylacetamide, TiO_2 (MCB reagent grade, particle size 125-250 μm) was added, the mixture stirred thoroughly and the solvent was then removed by evaporation. The reaction was studied with illumination from a 1.6 kW Xenon lamp with appropriate optical filters. The general procedure involved irradiation of 20 mL solution samples of 0.20 $\underline{M}$ Na_2SO_4 containing 2.0 m$\underline{M}$ hydroquinone and 0.200 g of photocatalyst in Pyrex tubes with continuous bubbling of oxygen. The amount of hydroquinone oxidized was determined by cyclic voltammetric analysis before and after irradiation. Typical results are given in Table 1. In control experiments 3 and 4 involving uncoated TiO_2 or H_2Pc-containing solutions irradiated with light of wavelength longer than 460 nm where TiO_2 shows no absorption but H_2Pc has strong absorption, very little oxidation of hydroquinone occurred. The photooxidation efficiency at long wavelengths (>460 nm) was, however, substantially enhanced by coating the phthalocyanines on TiO_2 powder (experiments 5 and 6). Accordingly, the photocatalytic activity at long wavelengths (>460 nm) is associated with the excitation of phthalocyanines and charge transfer at the interface between the phthalocyanine and TiO_2, i.e., it is spectrally sensitized.

The photocatalytic activity of suspended phthalocyanine-coated TiO_2 powder can be correlated with the photoelectrochemical behavior of n-type TiO_2 (rutile) single crystal electrodes covered with phthalocyanine thin films. As shown in Fig. 1, the photoinduced oxidation of hydroquinone on an illuminated H_2Pc-coated TiO_2 electrode takes place at more negative potentials than the reduction of oxygen on the TiO_2 electrode. Thus, the photooxidation of hydroquinone on phthalocyanine sites and the reduction of oxygen on TiO_2 sites can take place simultaneously on the same particle. As shown by the energy level scheme in Fig. 2, irradiation of an H_2Pc-coated TiO_2 particle with light of energy smaller than the band gap of TiO_2 but greater than the band gap of H_2Pc (∿2 eV)[16] causes excitation of an electron to the conduction band of H_2Pc leaving a hole in the valence band. The photogenerated holes are sufficiently energetic (∿0.8 V vs. NHE)[17] to oxidize hydroquinone while the photogenerated electrons are injected into the conduction band of TiO_2 leading to the reduction of oxygen.

Note that the photogenerated holes formed by the excitation of phthalocyanines are insufficiently energetic to oxidize H_2O or Cl^-. In the absence of hydroquinone or other reducing agents, the sensitized photocurrent showed a peak around -0.30 V vs. SCE (see curve c in Fig. 1) which decreased with time. This photocurrent is attributable to the photooxidation of phthalocyanines, which in the absence of reducing agents remains in the oxidized state. The addition of hydroquinone which acts as a "supersensitizer" is required to obtain a continuous current. The quantum efficiency for the photooxidation of hydroquinone at 632.8 nm under light intensity ∿50 mW/cm^2 was estimated to be about 0.1%. It is interesting to notice that different from the photocurrent peak shown in Fig. 1c for the H_2Pc-coated electrode, the peak photocurrent on the bare TiO_2 electrodes (d) was time-independent and was located at a slightly more positive potential (-0.22 V vs. SCE). The origin of this peak is not clear, but it probably involves the surface states of TiO_2.

The experiments described here demonstrate the feasibility of sensitized photoassisted redox reactions with phthalocyanine-coated semiconductor powders. Sensitized heterogeneous photocatalytic and photoelectrosynthetic processes employing other semiconducting substrate powders and other phthalocyanines are currently under investigation in this laboratory.[18]

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18. 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.

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Table 1. Sensitized Photocatalytic Oxidation of Hydroquinone in Oxygen-Saturated Solutions[a]

Exp. No.	Catalyst[b]	Time of Illumination (hrs)	Illumination Wavelengths	Hydroquinone Oxidized, (%)
1	TiO_2 (anatase)	4.0[c]	white light	< 1
2	TiO_2 (anatase)	4.0	white light	52
3	H_2Pc	23.0	> 460 nm	1
4	TiO_2 (anatase)	22.0	> 460 nm	3
5	TiO_2 (anatase)/H_2Pc [d]	22.5	> 460 nm	25
6	TiO_2 (anatase)/MgPc [d]	23.0	> 460 nm	17

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[a] 20 mL of 0.20 M Na_2SO_4 containing 2.0 mM hydroquinone.

[b] 200 mg. TiO_2 taken.

[c] Solution was deoxygenated thoroughly with N_2.

[d] TiO_2 was partially coated with about 2 mg. of the phthalocyanine from N,N'-dimethylacetamide solution.

Figure Captions

Fig. 1 Current-potential curves for n-type TiO_2 (rutile, single crystal) and metal-free phthalocyanine-coated n-type TiO_2 electrodes in the datk and under chopped illumination with 450 W Xe lamp fitted with a 590 nm cut-on filter. Curves a and b use the right-hand scale and curves c-e use the left-hand scale. The photocurrent was measured by phase-sensitive detection techniques. Cyclic voltammetry in the dark at TiO_2 in (a) deoxygenated and (b) oxygen-saturated 0.25 M Na_2SO_4, 0.025 M phosphate buffer (pH $\underset{\sim}{}$ 6.9). Scan rate, 100 mV/sec. Initial potential +0.60 V vs. SCE. (c) Current potential curve under illumination at H_2Pc-coated TiO_2 electrodes in deoxygenated 0.25 M Na_2SO_4, 0.025 M phosphate buffer (pH $\underset{\sim}{}$ 6.9) or 0.50 M KCl, 0.025 M phosphate buffer (pH $\underset{\sim}{}$ 6.9). H_2Pc film thickness ∿500 Å. Scan rate, 5 mV/sec. Initial potential -0.37 V vs. SCE. (d) Current-potential curve under illumination at TiO_2 in deoxygenated 0.25 M Na_2SO_4, 0.025 M phosphate buffer (pH $\underset{\sim}{}$ 6.9) with or without 0.50 mM hydroquinone. Scan rate, 5 mV/sec. Initial potential -0.28 V vs. SCE. (e) Current-potential curve under illumination at H_2Pc-coated TiO_2 electrodes in deoxygenated 0.25 M Na_2SO_4, 0.025 M phosphate buffer (pH $\underset{\sim}{}$ 6.9) containing 0.50 mM hydroquinone. H_2Pc film thickness ∿500 Å. Scan rate, 5 mV/sec. Initial potential -0.45 V vs. SCE. s denotes the potential at which the scan was initiated.

Fig. 2 Schematic diagram for the electron transfer at H_2Pc on TiO_2. E_{CB} and E_{VB} denote the potentials of the conduction band edge and the valence band edge of TiO_2. E_{CB}' and E_{VB}' are the corresponding potentials for H_2Pc. Redox potential for p-hydroquinone (H_2Q)/p-benzoquinone (BQ) is shown on the right.

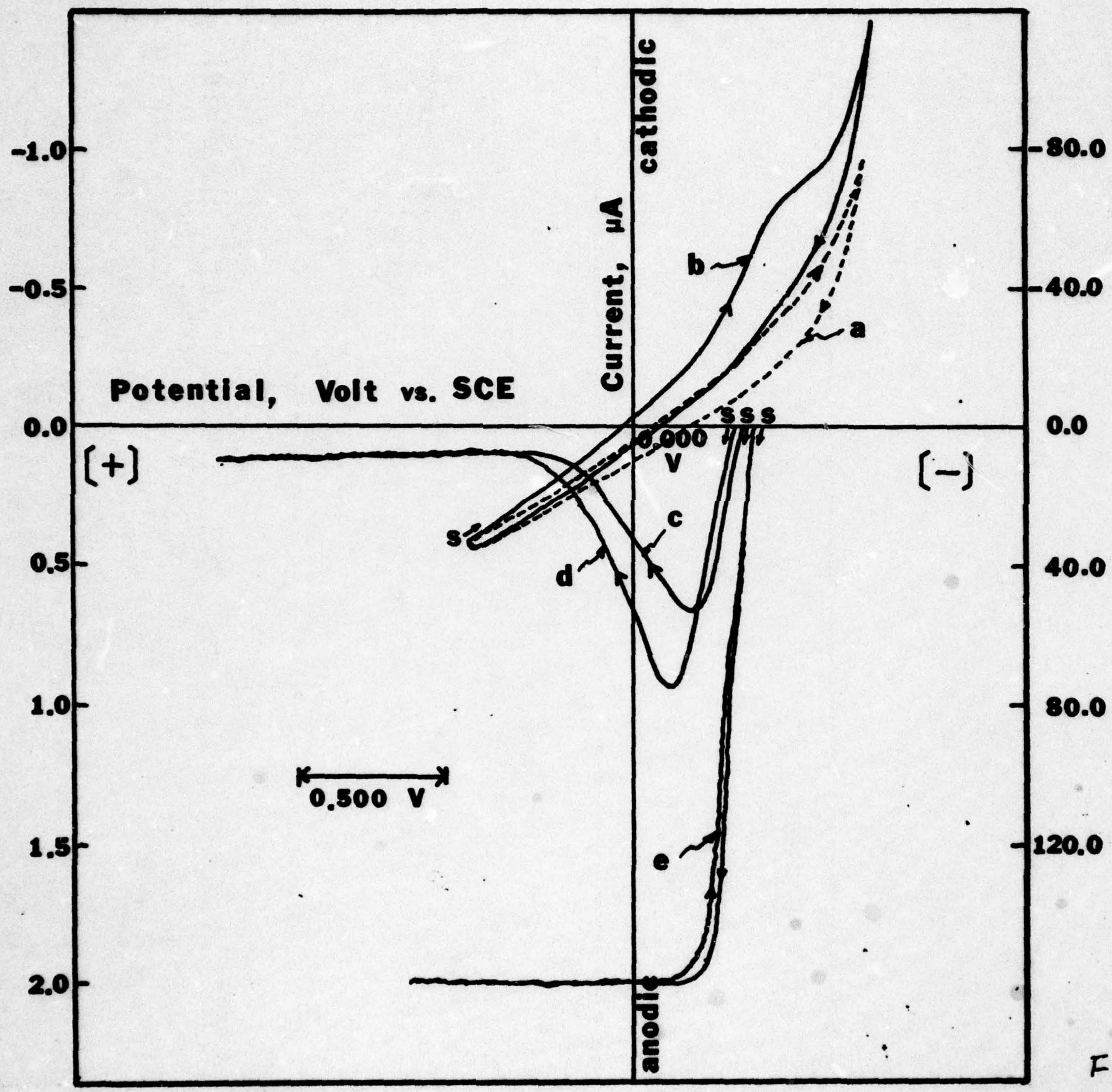
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Fig. 1

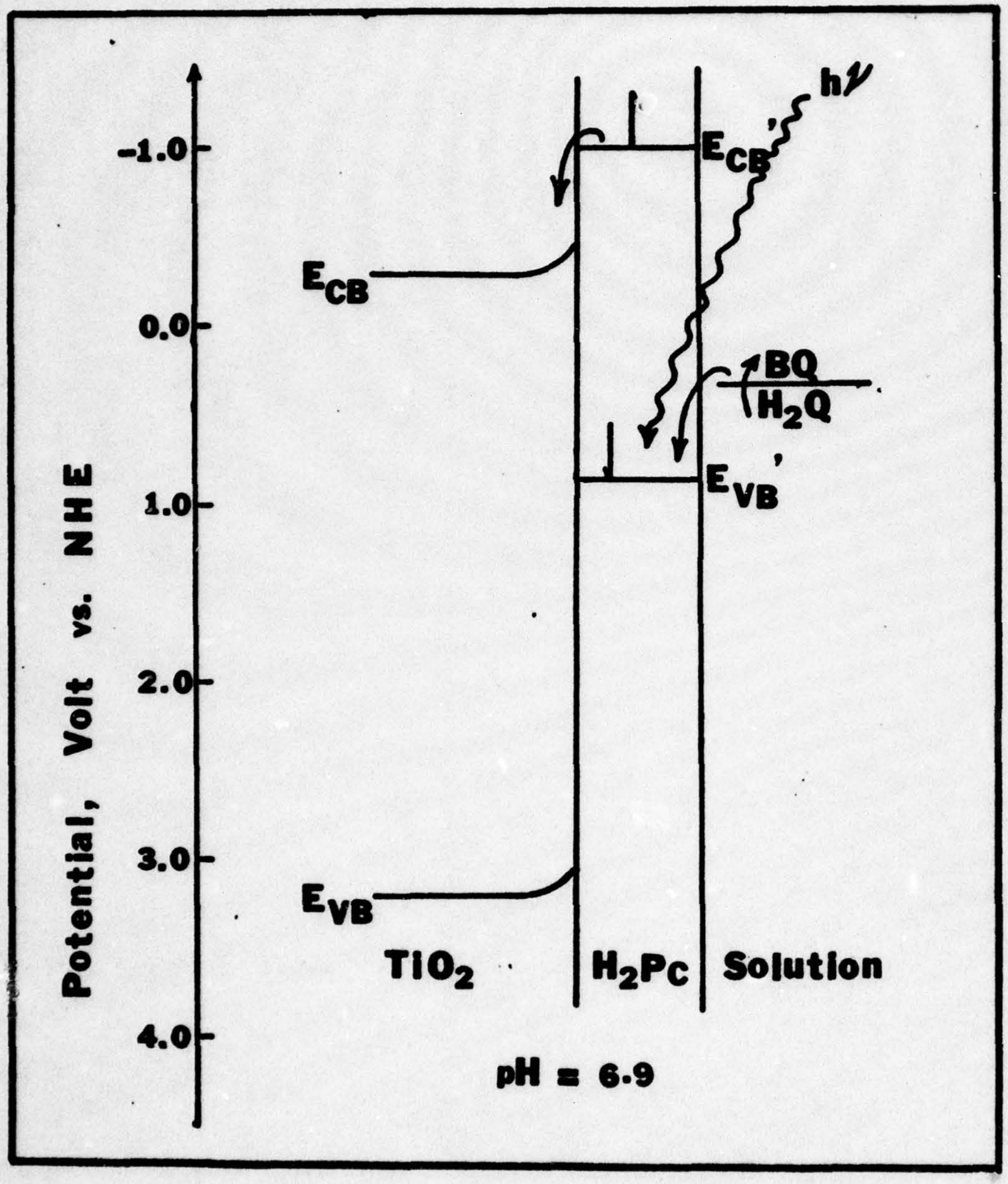
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Fig. 2

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