# Spectral sensitization of the heterogeneous photocatalytic oxidation of hydroquinone in aqueous solutions at phthalocyanine-coated titanium dioxide powders

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

| expt | catalyst[b] | time of illumination, h | 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$_2$Pc | 23.0 | >460 nm | 1 |
| 4 | TiO$_2$ (anatase) | 22.0 | >460 nm | 3 |
| 5 | TiO$_2$ (anatase)/ H$_2$Pc[d] | 22.5 | >460 nm | 25 |
| 6 | TiO$_2$ (anatase)/ MgPc[d] | 23.0 | >460 nm | 17 |

[a] 20 mL of 0.20 M Na$_2$SO$_4$ containing 2.0 mM hydroquinone. [b] 200 mg of TiO$_2$ taken. [c] Solution was deoxygenated thoroughly with N$_2$. [d] TiO$_2$ was partially coated with ~2 mg of the phthalocyanine from N,N'-dimethylacetamide solution.

## 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 2-propanol 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$_2$Pc) or magnesium phthalocyanine (MgPc), were dissolved in N,N'-dimethylacetamide, TiO$_2$ (MCB reagent grade, particle size 125–250 $\mu$m) was added, the mixture was 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 M Na$_2$SO$_4$ containing 2.0 mM 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 I. In control experiments 3 and 4 involving uncoated TiO$_2$ or H$_2$Pc-containing solutions irradiated with light of wavelength longer than 460 nm where TiO$_2$ shows no absorption but H$_2$Pc has
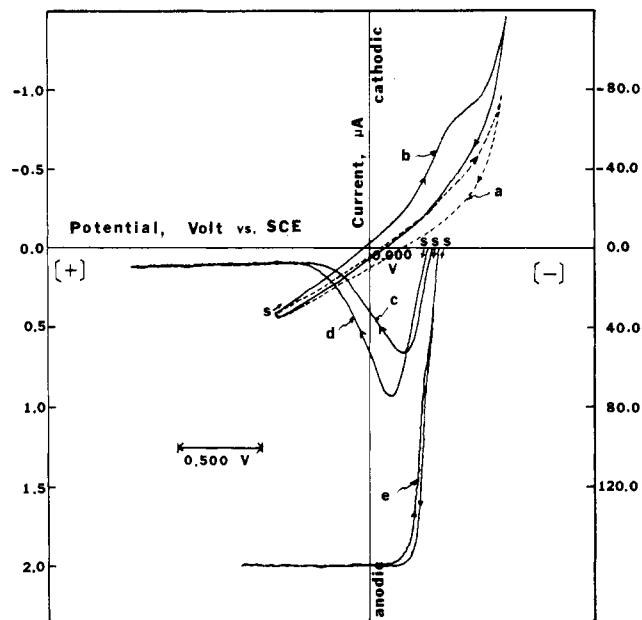


Figure 1. Current-potential curves for n-type TiO$_2$ (rutile, single crystal) and metal-free phthalocyanine-coated n-type TiO$_2$ electrodes in the dark and under chopped illumination with 450-W Xe lamp fitted with a 590-nm cut-on filter. Curves a and b use the right-hand scale and curves c–e use the 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$_2$SO$_4$, 0.025 M phosphate buffer (pH ≃6.9) (scan rate, 100 mV/s; initial potential, +0.60 V vs. SCE). (c) Current-potential curve under illumination at H$_2$Pc-coated TiO$_2$ electrodes in deoxygenated 0.25 M Na$_2$SO$_4$, 0.025 M phosphate buffer (pH ≃6.9) or 0.50 M KCl, 0.025 M phosphate buffer (pH ≃6.9) (H$_2$Pc film thickness, ~500 Å; scan rate, 5 mV/s; initial potential, −0.37 V vs. SCE). (d) Current-potential curve under illumination at TiO$_2$ in deoxygenated 0.25 M Na$_2$SO$_4$, 0.025 M phosphate buffer (pH ≃6.9) with or without 0.50 mM hydroquinone (scan rate, 5 mV/s; initial potential, −0.28 V vs. SCE). (e) Current-potential curve under illumination at H$_2$Pc-coated TiO$_2$ electrodes in deoxygenated 0.25 M Na$_2$SO$_4$, 0.025 M phosphate buffer (pH ≃6.9) containing 0.50 mM hydroquinone (H$_2$Pc film thickness, ~500 Å; scan rate, 5 mV/s; initial potential, −0.45 V vs. SCE). s denotes the potential at which the scan was initiated.

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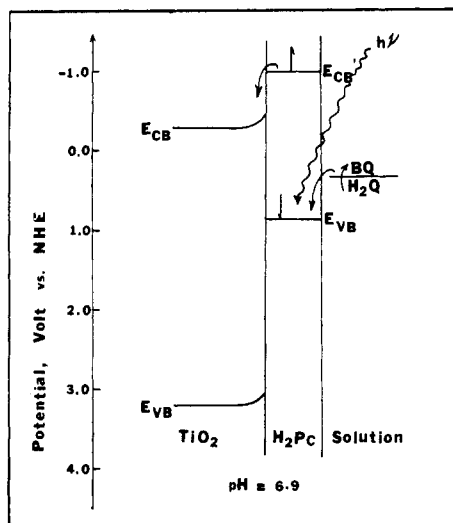
**Figure 2.** Schematic diagram for the electron transfer at $H_2Pc$ on $TiO_2$. $E_{CB}$ and $E_{VB}$ denote the potentials of the conduction band edge and the valence band edge of $TiO_2$. $E_{CB}'$ and $E_{VB}'$ are the corresponding potentials for $H_2Pc$. Redox potential for *p*-hydroquinone $(H_2Q)$/*p*-benzoquinone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

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 Figure 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 Figure 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 $H_2Pc$ ($\sim$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 ($\sim$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 Figure 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 of $\sim$50 mW/cm$^2$ was estimated to be $\sim$0.1%. It is interesting to notice that, different from the photocurrent peak shown in Figure 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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## Free-Energy Relationships for Electron-Transfer Processes

*Sir:*

Following the absolute reaction-rate theory, the rate constant of an outer-sphere electron-transfer (ET) reaction (eq 1) is given in eq 2 where $A$ is the frequency factor and $\Delta G^{\ddagger}$ is the free energy of activation. At least three different relationships between the free energy of activation, $\Delta G^{\ddagger}$, and the standard free-energy change, $\Delta G$, are currently used to discuss the results obtained in homogeneous series of ET reactions.

$$M + N \xrightarrow{k} M^+ + N^- \tag{1}$$
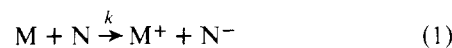
$$k = Ae^{-\Delta G^{\ddagger}/RT} \tag{2}$$

(i) One is the Marcus equation[1] (eq 3) where $\Delta G^{\ddagger}(0)$ is the so-called "intrinsic barrier", i.e., the free energy of activation for a reaction with $\Delta G = 0$:

$$\Delta G^{\ddagger} = \Delta G^{\ddagger}(0)[1 + (\Delta G/4\Delta G^{\ddagger}(0))]^2 \tag{3}$$

(ii) There are linear free-energy relationships (eq 4) of the type discussed by Brønsted and Pedersen[2] and by Polanyi et al.,[3] where $\alpha$ and $\beta$ are two empirical parameters:

$$\Delta G^{\ddagger} = \alpha \Delta G + \beta \tag{4}$$

(iii) The third is the empirical relationship (eq 5) first proposed by Rehm and Weller (RW),[4] where $\Delta G^{\ddagger}(0)$ has the same meaning as in eq 3:

$$\Delta G^{\ddagger} = \frac{\Delta G}{2} + \left\{ \left(\frac{\Delta G}{2}\right)^2 + [\Delta G^{\ddagger}(0)]^2 \right\}^{1/2} \tag{5}$$

It is the purpose of this letter to discuss some aspects of these relationships and to suggest the use of another one first derived by Marcus[5] for atom- and proton-transfer reactions and more recently obtained by Agmon and Levine[6] on the basis of a