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Characterization of Particulate Titanium Dioxide Photocatalysts by Photoelectrophoretic and Electrochemical Measurements

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Abstract: The electrophoretic mobility of TiO_2 particles was determined in the dark and under illumination in aqueous solutions as a function of pH. The results show that in the absence of an easily reducible species in solution, irradiation causes a buildup of negative charge on the particle surface. Platinized TiO_2 powders do not exhibit this effect. Electrochemical measurements on TiO_2 powder suspensions at Pt and In_2O_3 electrodes show photoinduced anodic currents. The action spectra for the TiO_2 particles ($E_g = 3.1$ eV) and the potentials for the photogenerated electrons (~ -0.46 V vs. NHE) can be obtained from these measurements.

Introduction

Semiconductor powders suspended in liquid solutions have been employed as photocatalysts in a number of reactions, such as the oxidation of CN^- with O_2 at TiO_2,[1] the decomposition of acetic acid at platinized TiO_2,[2] and a number of other processes.[3] These reactions are thought to occur by the absorption of light in the semiconductor to form an electron-hole (e^-, h^+) pair. Reactions of these photogenerated species with solution species at the particle surface lead to the products of the photoredox reaction. The capture of holes by reductants in solution and of electrons by oxidants have been described by an electrochemical model[1-3] in which the steady-state redox half-reactions must occur at a potential where the anodic and cathodic currents (i.e., rates per unit area) are equal. Such a model has been useful in designing such particulate systems, for example, by employing platinum as a catalyst to facilitate the reduction of protons as a half-reaction.[2b]

The characterization of these reactions by product analysis and rate determination is straightforward, but few methods exist for probing the details of the reaction mechanisms or the catalyst properties in situ. The powders themselves can be examined by photoacoustic or reflectance spectroscopic techniques to determine the energy of the band gap. Spin trapping has been employed to identify intermediate radicals formed in these processes.[4] We describe here two techniques which allow characterization of the powders during the photoreaction and provide evidence for the charge generation steps and the proposed electrochemical model for these processes.

The first approach is based on electrophoresis of the particles during the photocatalytic reaction.[5] Electrophoresis is the movement of charged particles in a suspension resulting from an applied electric field.[6] The electrophoretic mobility, u, is the velocity of a particle per unit field strength. In the usual electrophoretic measurement, the particles acquire a net surface charge as a result of dissociation equilibria of surface charge groups or by specific adsorption of ions from solution. A suspended particulate system must be electrically neutral overall; however, the particle dimensions are much larger than those of the solvated ions so that an effective surface charge can exist that is considerably greater than that of a solution species. Consequently, an electrical double layer is formed with an excess of counterions in the vicinity of the particle. The experimentally measurable feature is the potential at the shearing plane which is associated with the particle/solution interface, defined as the zeta potential, ζ.[6] However, in addition to this ionic charge at the particle surface, electronic charge (excess e^- or h^+) can also exist and contribute to the net particle charge. For example, if photogenerated holes can react with a solution reductant but the electrons do not react, a net negative charge will build up on the particles. Determination of the electrophoretic mobility of suspended powders (e.g., TiO_2) thus provides a measure of the net surface charge and illustrates the change in surface charge which results from a photoredox reaction.

We also demonstrate here that the photogenerated electronic charges on the particles can be collected at an electrode.[7] This allows rather straightforward electrochemical measurements to be made on the suspended semiconductor powders which yield information not only about the action spectra and the nature of the charges but also about their energies.

Experimental Section

Materials. The titanium dioxide powder was purchased from Matheson, Coleman, and Bell in the anatase form. The X-ray diffraction spectra contained the characteristic anatase peak at 25.2° 2θ (3.52 Å), and the principal rutile peak at 27.3° 2θ (3.25 Å) was absent.[8] The surface area, measured by the BET method was approximately 15 m^2/g (Micrometrics Model 2100 D, Surface Area-Pore Volume Analyzer.) Powders referred to as "reduced" were pretreated under H_2 at 500 °C for 8 h. Platinized catalysts were prepared by the photocatalytic reduction method previously reported by this laboratory[9] and contained about 10% Pt by weight. All solutions for electrophoresis measurements were prepared from reagent grade chemicals with concentrations adjusted so that the ionic strength was 0.02 M. Solutions of 0.02 M HCl and 0.02 M NaOH were used as media at pH 1.7 and 12.3, respectively, and 0.02 M KCl solutions adjusted with 0.02 M HCl or NaOH were used for intermediate pH values. For measurements in sulfate media, 6.7×10^{-3} M Na_2SO_4 solutions were employed. All solutions were deaerated with N_2 for a minimum of 4 h prior to measurement. An equilibration time of at least 12 h was required for the suspended particulates to reach a constant mobility.

Apparatus. Electrophoresis measurements generally followed the usual microelectrophoresis practice and were made in a three-compartment Pyrex cell (Figure 1). A long, thin cylindrical capillary (radius, R = 0.65 mm) was used to produce a uniform electric field. Ag|AgCl electrodes were used to provide nongassing conditions even at large applied potentials (100 V dc). An Olympus microscope at 100x power was used for all mobility measurements. Potentials were applied by a Kepco voltage regulated power supply. Voltage measurements were made with

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(1) Frank, S. N.; Bard, A. J. *J. Phys. Chem.* **1977**, *81*, 1484.

(2) (a) Kraeutler, B.; Bard, A. J. *J. Am. Chem. Soc.* **1978**, *100*, 2239. (b) Kraeutler, B.; Bard, A. J. *Ibid.* **1978**, *100*, 5985.

(3) (a) Bard, A. J. *J. Photochem.* **1979**, *10*, 59; (b) Bard, A. J. *Science* **1980**, *207*, 139.

(4) (a) Kraeutler, B.; Jaeger, C. D.; Bard, A. J. *J. Am. Chem. Soc.* **1978**, *100*, 4903; (b) Jaeger, C. D.; Bard, A. J. *J. Phys. Chem.* **1979**, *83*, 3146; (c) Harbour, J. R.; Hair, M. L. *Ibid.* **1977**, *81*, 1791; (d) *Ibid.* **1979**, *83*, 652.

(5) See, for example: (a) Takahashi, A.; Aikawa, Y.; Toyoshima, Y.; Sukigara, M. *J. Phys. Chem.* **1979**, *83*, 2854; (b) Oppenheim, R. C.; Buchanan, A. S.; Healy, T. W. *Aust. J. Chem.* **1967**, *20*, 1743, and references therein.

(6) Detailed treatments of electrophoresis measurements and the interpretation of these effects are contained in (a) Shaw, D. J. "Electrophoresis"; Academic Press: New York, 1969; (b) Abramson, A. H. et al. "The Electrophoresis of Proteins and the Chemistry of Cell Surfaces"; Reinhold: New York, 1942.

(7) Dunn, W.; Aikawa, Y.; Bard, A. J. *J. Electrochem. Soc.*, in press.

(8) X-ray Data Files, American Society for Testing Materials, Philadelphia, Penn., 1958. No. 21-1272 (anatase); No. 21-1276 (rutile).

(9) Kraeutler, B.; Bard, A. J. *J. Am. Chem. Soc.* **1978**, *100*, 4317.

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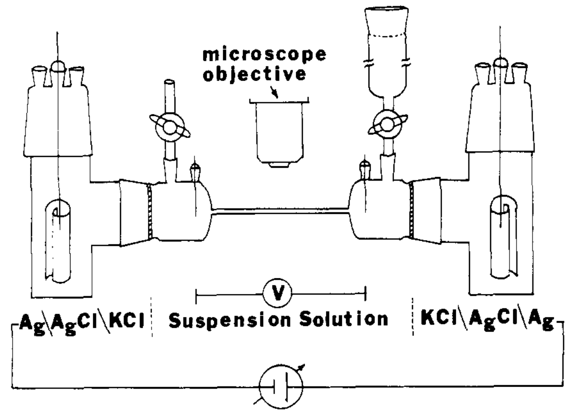

Figure 1. Photoelectrophoresis measurement cell.

a Keithley 179 TRMS digital voltmeter.

Electrochemical measurements were made in a two-compartment Pyrex cell divided by a fine glass frit. The Pt electrodes, area 2 cm^2, were polished and cleaned in concentrated nitric acid to remove any oxide layer. Measurements involving n-TiO_2 suspensions were made with the semiconductor powder in one compartment only. Current-potential curves were recorded with a Princeton Applied Research (PAR) Model 173 potentiostat/galvanostat, a PAR Model 175 universal programmer, and a Houston Instruments Model 2000 recorder. The illumination source was a 2.5-kW xenon lamp (Christie Corp., Los Angeles, Calif., Model UF 30 KK) operated at 1.6 kW. A fused silica fiber optic (Voltec Fiber Optics, West Boylston, Mass.) was used to direct the light onto the capillary. The light intensity thus provided to the electrophoresis cell was approximately 3.5 mW/cm^2 and illuminated a 1-cm length of the capillary tube.

Method of Electrophoresis Measurements. The velocity, v, of a suspended particle moving in an electric field is related to the applied field, E, by[6]

$$v = uE \tag{1}$$

where u is the electrophoretic mobility of the particle. The surface charge on the particle is equal in magnitude but opposite in sign to the sum of charges in the solution fixed and diffuse double layers. When an external field is applied, the migration velocity of the suspended particle is the result of the potential at the plane of shear, the zeta potential, ζ. The relation between the mobility and the potential was given by von Smoluchowski as[6,10]

$$u = +\epsilon\zeta/\eta \tag{2}$$

where $\epsilon = e_r\epsilon_0$, is the dielectric constant, and η is the viscosity of the liquid. This equation assumes that all radii of curvature on the particle surface are much larger than the thickness of the electrical double layer. Hückel[11] proposed

$$u = \frac{+2}{3}\frac{\epsilon\zeta}{\eta} \tag{3}$$

for small particles. Because of the liquid movement that occurs in the applied field (electroosmosis), the measured velocity in the capillary represents the sum of the liquid velocity and the particle velocity against the liquid. The liquid velocity due to electroosmosis depends on the distance, r, from the center of the cylinder, since the distribution of liquid velocities in the capillary has cylindrical symmetry. Therefore, the observed velocity of the particle is the sum of the electrophoretic velocity and the velocity of the liquid, v_{EO}:

$$v_{EO}(r) = 2v_0(r)\left[\left(\frac{r}{R}\right)^2 - \frac{1}{2}\right] \tag{4}$$

where R is the radius of the capillary and v_0 is the velocity of the liquid at the capillary wall. To correct for the liquid velocity, measurements of particle velocity are made at different values of r, determined by measuring the distance from the top inside wall of the capillary with the calibrated fine adjustment of the microscope. From eq 3, at the level where $(r/R)^2 = 1/2$, $v_{EO} = 0$, so that the measured velocity is equal to the actual electrophoetic velocity of the particle. This level, which occurs at $r = 0.707R$, is called the stationary level. The velocity of the particle was measured at different values for the electric field and the mobility was determined from the slope of the v-E curve, via eq 1.

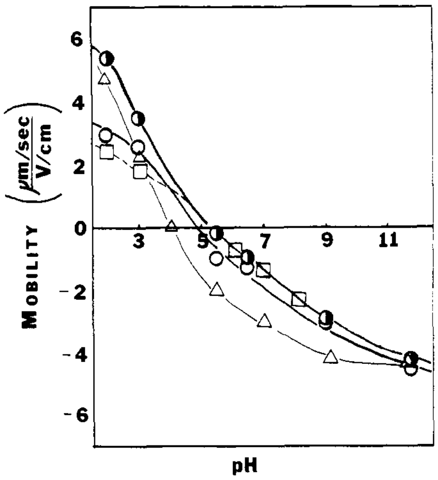

Figure 2. Variation of electrophoretic mobility with pH (ionic strength = 0.02 M): (◑) TiO_2, dark, chloride media; (○) TiO_2, light, chloride media; (□) Pt/TiO_2, light and dark, sulfate media; (△) Pt/TiO_2, light and dark, chloride media.

Results and Discussion

Electrophoretic Measurements. TiO_2. Measurements of the mobility of suspended TiO_2 particles were made as a function of pH in aqueous solutions of ionic strength 0.020 M; the results are shown in Figure 2. In the dark, the net surface charge on the particle surface is the result of adsorption of protons or hydroxyl ions; these ions are usually the potential-determining ions at metal oxide sols.[6a,12] In acidic solutions, protonation of the surface oxide produces a net positive charge and the particle moves in the direction of the field toward the negative electrode. Conversely, at higher pH values, adsorption of hydroxyl ion produces a negative surface charge. The isoelectric point or the pH of zero ζ potential, pH_{zzp}, for the n-TiO_2 particles occurs at 5.35. This result is in general agreement with previous measurements on TiO_2;[12,13] the properties of this material are known to depend on the method of preparation and pretreatment.

The effect of illumination of the TiO_2 suspension on the mobility is also shown in Figure 2. At all pH values, irradiation of the particles with the xenon lamp causes the mobility to change in a direction that indicates formation of negative charge on the particle surface. This is consistent with the model for photoprocesses at the TiO_2 particle. Irradiation with light of energy greater than the band gap produces an electron-hole pair. The photogenerated hole is sufficiently energetic to cause oxidation of water (probably via intermediate hydroxyl radicals). However, in the absence of oxygen or other easily reducible species, the photogenerated electrons accumulate on the TiO_2 particles. While the potential of the electrons, at least initially, is such that some proton reduction can occur, the rate of this reaction at the TiO_2 surface is slow. Thus, the observed direction of charging of the particles demonstrates that the rate of oxidation at the illuminated particle surface is much greater than the rate of reduction. After the illumination was stopped, the measured value of the mobility remained the same as that determined in the light for several minutes and then gradually decayed to the value in the dark. Thus, the excess negative surface charge does not decay rapidly, consistent with a slow reduction process at the TiO_2 surface. The small area of the capillary that is illuminated and the movement of particles out of this area made this rate of charge decay difficult to quantify.

Pt/TiO_2. The general behavior of the platinized TiO_2 (Pt/TiO_2) was somewhat different. As shown in Figure 2, at any given pH, the mobility is more negative than that of unplatinized powder. Chloride ion is known to adsorb quite strongly on Pt,[14] and this

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(10) Smoluchowski, M. von *Bull. Acad. Sci. Cracovie* **1903**, 182.

(11) Debye, P.; Hückel, E. *Phys. Z.* **1924**, *25*, 97.

(12) Berube, Y. G.; De Bruyn, P. L. *J. Colloid Interface Sci.* **1968**, *27*, 305.

(13) Johansen, P. G.; Buchanan, A. S. *Aust J. Chem.* **1957**, *10*, 398.

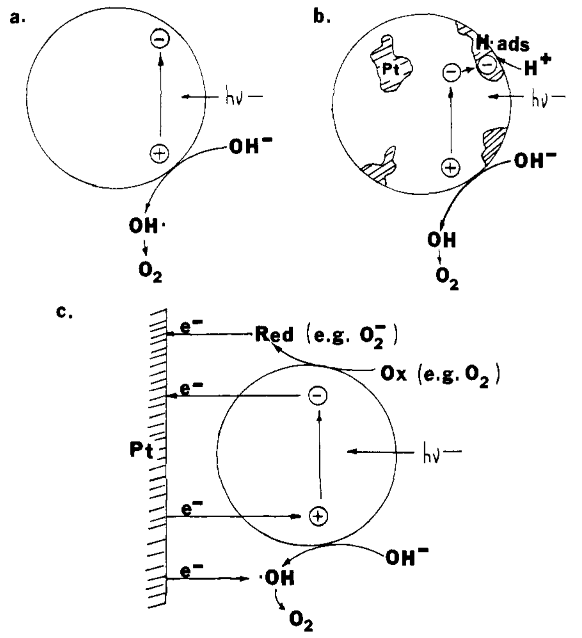

Figure 3. Schematic diagram photoredox reaction mechanisms: (a) TiO_2 in 0.02 M HCl, (b) Pt/TiO_2 in 0.02 M HCl, (c) TiO_2 in 0.02 M HCl at Pt electrode.

probably leads to the observed increased negative surface charge on the particles. Sulfate ion is less strongly adsorbed on Pt[14] and in sulfate media the Pt/TiO_2 shows essentially the same mobility as TiO_2 alone, except at low pH values where adsorption of HSO_4^- may occur. Under illumination, the Pt/TiO_2 particles showed the same mobility as in the dark. This lack of photoeffect can be explained by the more rapid reduction of protons by the photogenerated electrons at the Pt as has been demonstrated in studies of the photodecarboxylation of acetic acid.[2] When the rates of the oxidation and reduction reactions (i.e., the anodic and cathodic current densities) at the particle surface are initially essentially equal, no buildup of electronic charge occurs. A schematic representation of the processes at an illuminated powder is given in Figure 3a and 3b.

Electrochemical Measurements. The photogenerated electronic charge on the particles can be collected at an inert electrode immersed in the suspension; that is, electrochemical measurements of the suspended powders are possible.[7] When a Pt-working electrode in a three-electrode cell is immersed in a carefully deaerated solution of 0.02 M HCl in the absence of the TiO_2 held at a potential of +0.40 V vs. SCE and irradiated, only very small currents are observed (Figure 4a). The origin of these is unknown and was not investigated further; very small photoeffects on metal electrodes have previously been attributed to oxide films on the surface or to thermal promotion of faradaic processes. When the same experiment is carried out in the presence of a TiO_2 suspension (Figure 4b), a large cathodic transient which quickly decays to a steady-state anodic current is observed. When the light is turned off, the current shows a small anodic spike and then decays. When oxygen is present in the solution, no photoinduced anodic current is observed. To ensure that the observed photoinduced current could be observed without an externally applied potential, experiments were also carried out in a two-electrode cell (Figure 5). Oxygen was removed from the compartment containing the TiO_2 suspension but not from the other compartment containing the Pt counter electrode. When the TiO_2 slurry compartment was illuminated and the short circuit current (measured with a current follower) was determined, a steady-state anodic current was observed (Figure 4c). If the Pt electrode was turned so that the surface of the Pt electrode was parallel to the light beam, the anodic current was essentially the same as that produced when the full area of the electrode was irradiated. The initial current pulse in the cathodic direction was also unaltered by change in the orientation of the electrode in the light beam. When the incident light intensity was varied with neutral density filters, the current was found to be proportional to the light intensity. These results suggest that the current originates with TiO_2 particles suspended in the solution rather than an adsorbed layer of particles on the electrode surface. When the suspension is stirred during the irradiation (Figure 4c), the initial cathodic current is unchanged, but the steady-state anodic current was slightly smaller. Increased light scattering by the stirred slurry may result in a lower light intensity in the vicinity of the electrode, thus causing a reduction in the observed photocurrent.

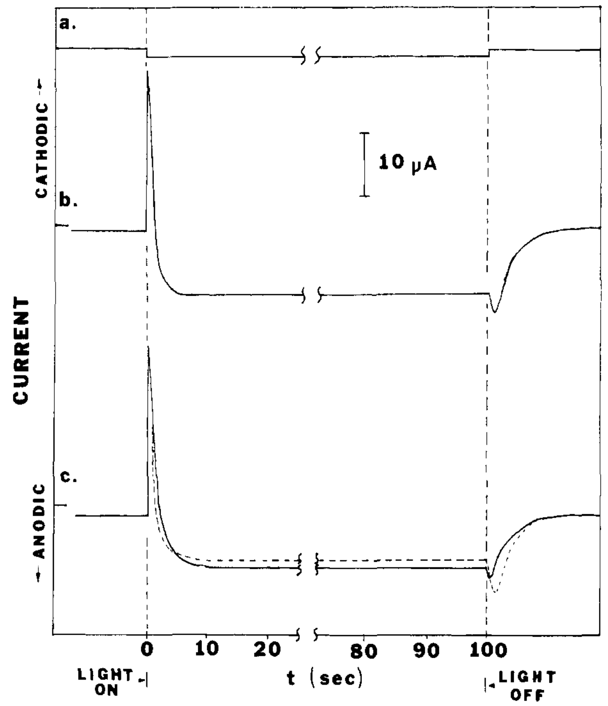

Figure 4. Photocurrent response in 0.02 M HCl of (a) Pt electrode, (b) TiO_2 slurry at Pt electrode, (c) TiO_2 slurry at Pt electrode in two-electrode cell (Figure 5); (---) stirred, (—) unstirred.

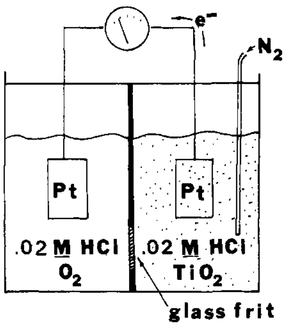

Figure 5. TiO_2 slurry electrode, two-electrode cell configuration.

These electrochemical effects can be explained by the model used in the photocatalysts and photoelectrophoresis studies (Figure 3c). Cathodic currents arise from electron flow from the electrode to holes or to intermediates formed on oxidation (e.g., OH·) at the particle surface, while anodic currents represent discharge of photogenerated electrons or reduced intermediates. The initial cathodic pulse probably represents a somewhat faster rate for discharge of oxidized intermediates. However, these decay in a following reaction and the buildup of electrons leads to a net anodic current at steady state. A simple kinetic model, to be described

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(14) See, for example, Balashova, N. A.; Kazarinov, V. E. *Electroanal. Chem.* **1969**, *3*, 135, and references therein.

(15) The currents seen with a bare Pt electrode depend on the surface preparation. At an unpolished or oxidized electrode, somewhat larger transients are found.

(16) Dutoit, E. C.; Cardon, F.; Gomes, W. P. *Ber. Bunsenges. Phys. Chem.* **1976**, *80*, 475.

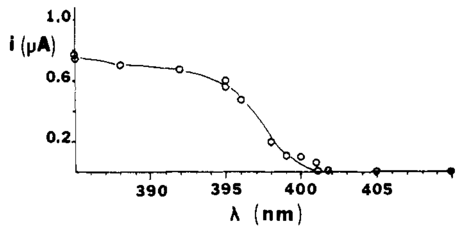

Figure 6. Action spectrum of TiO_2 slurry electrode at Pt in 0.02 M HCl, 1 M acetic acid.

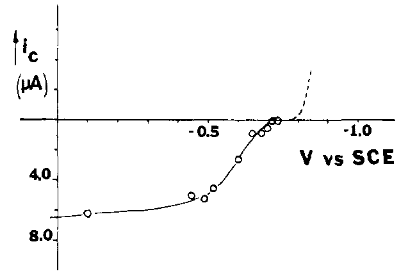

Figure 7. (—) Photocurrent–voltage response of TiO_2 slurry electrode at In_2O_3: 80 mg of TiO_2 in 0.025 M HCl, 1 M acetic acid. (---) H_2 evolution at In_2O_3.

in detail elsewhere, allows simulation of the observed photocurrent–time behavior by the appropriate choice of rate constants for the different electron-transfer processes. Moreover, the cathodic current transient is suppressed completely when the same experiment is carried out in a solution containing 2.2 M acetic acid. Previous studies have shown that the photogenerated holes are efficiently scavenged by acetate with the production of methyl radicals that rapidly decay. Thus, the addition of acetate removes the production of appreciable amounts of reducible intermediate at the particle surface and hence greatly decreases the cathodic current. Similarly, studies with CdS suspensions, to be discussed elsewhere, show no cathodic transients. In this case, the holes produce Cd^{2+} and S which are not readily reducible at Pt at the applied potential.

These electrochemical methods are especially useful in determining the action spectra and energy levels of carriers in the powders. The measured photoresponse for a TiO_2 suspension at a Pt electrode in 1 M acetic acid solution at +0.100 V vs. SCE determined by measuring transients at fixed wavelengths is shown in Figure 6. The onset of photocurrent is consistent with a band gap, E_g, of 3.1 eV. The potential dependence of the anodic photocurrent under xenon lamp irradiation at an In_2O_3 conductive glass electrode is shown in Figure 7. The In_2O_3 electrode was used because it shows a high hydrogen overpotential and allows investigation of a region out to rather negative potentials. The anodic photocurrent onset occurs at about −0.70 V vs. SCE (−0.46 V vs. NHE). This value is significantly more negative than the flat-band potential found with single-crystal rutile electrodes at this pH. If this represents the energy level of electrons in the powder, then these are more reducing than conduction band electrons in rutile. While further measurements must be undertaken to elucidate this behavior, these results suggest that electrochemical measurements of semiconductor powders in the dark and under illumination can aid in the characterization of these materials.

Conclusions

The results presented here clearly reinforce the proposed model for heterogeneous photoprocesses at semiconductor powders. The charge produced at the powders at steady state can be estimated from the electrophoresis measurements based on the usual assumptions[6] identifying the ζ potential as that at the outer Helmholtz plane (ϕ_2). Thus, from eq 2 and the relation between ϕ_2 and charge density, σ, in $\mu C\ cm^{-2}$, one obtains:[6]

$$\sigma = 11.7C^{1/2} \sinh (0.25\ zu) \qquad (5)$$

for water at 25 °C, where C is the concentration of the z:z electrolyte (M). Thus, for example, in the solutions at pH 1.7, the dark mobility of 5.3 $\mu m \cdot s^{-1}/V \cdot cm^{-1}$ leads to $\sigma = 2.9\ \mu C\ cm^{-2}$. This value agrees quite well with that obtained from adsorption isotherms obtained by titration of TiO_2 suspensions,[12] where the adsorption density of H^+ in acidic solutions $\sim 4 \times 10^{-11}$ mol cm^{-2} (equivalent to $\sim 4\ \mu C\ cm^{-2}$) was reported. Under irradiation the mobility decreased to 3.0 $\mu m \cdot s^{-1}/V \cdot cm^{-1}$. If one can assume that the total measured change in charge density corresponds to electronic charge, this represents electronic charge buildup of 1.5 $\mu C\ cm^{-2}$. Taking 20–50 $\mu F\ cm^{-2}$ as the capacitance of the inner layer at the powder,[17] we calculate a potential shift attributable to electronic charging of 30–75 mV. This shift is sufficiently small that the electronic charge production probably does not perturb the amounts of adsorbed ionic species to a significant extent. This number is of interest, however, because it extends the electrochemical model for processes at the semiconductor particle previously proposed. In the absence of an oxidizing agent in the solution, the particle under illumination initially attains a potential where the photooxidation reaction can be sustained. However, the charging process causes the potential to shift toward negative values, causing a decay in the partial anodic current and a decrease in the rate of the reaction at the particle surface. The role of a solution oxidant can then be viewed as the maintenance of the potential at values where the oxidation reaction can be sustained.

The direct electrochemical measurements on the semiconductor powders provide a rapid method of characterizing these materials in situ. This technique may also be useful in the examination of other types of liquid-phase heterogeneous redox catalysts. Such studies are in progress.

Acknowledgment. The support of this research by the National Science Foundation CHE 8000682) and the Robert A. Welch Foundation is gratefully acknowledged. We are indebted to Professor Donald Levin for the loan of the microscope and to John Somerville for construction of the electrophoresis cell.

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(17) Hunter, R. J.; Wright, H. J. L. *J. Colloid Interface Sci.* **1971**, *37*, 564.