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Photocurrent Enhancement via Trapping of Photogenerated Electrons of TiO_2 Particles

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The photocurrents derived from TiO_2 suspensions are enhanced when reducible species such as Cu^{2+} and Fe^{3+} are added to cells containing these suspensions. This process is proposed to occur via trapping of photogenerated electrons in the TiO_2 by these solution species, thereby reducing the extent of deleterious electron-hole recombination. The ability of platinum deposits on TiO_2 particles to participate in electron trapping and enhance photocurrent via formation of Pt-H species was demonstrated by electrochemical detection of adsorbed H on irradiated Pt/TiO_2.

Introduction

The utility of irradiated suspensions of semiconducting powders such as TiO_2, CdS, and WO_3 has been demonstrated in numerous photocatalytic and photosynthetic reactions.[1-7] In most of these reports the reactions were monitored by recording the rate of disappearance of reactant or formation of products. Additionally, physical methods have been employed to probe the energetics and mechanisms of reactions that occur in these systems. These include electron spin resonance-spin trapping techniques,[8,9] photoelectrophoresis,[10,11] and conductivity measurements.[12] Recently, reports have described how the photogenerated charge on TiO_2 particles could be collected at an inert collector electrode immersed in semiconductor powder suspensions.[10,13,14] By performing electrochemical studies of irradiated suspensions of semiconductor powders and studying the photocurrents as functions of time, irradiation wavelength and intensity, and collector electrode potential, one can obtain information about the energetics and kinetics of the relevant processes on the particles. Practical application of such semiconductor slurry electrodes might also be possible. Although easily measurable anodic photocurrents from TiO_2 suspensions were observed, the magnitude of the photocurrents was probably limited by rapid electron-hole (e^-h^+) recombination as photogenerated charges accumulated either on the surface or within the particle. Thus, the anodic photocurrent is increased by the addition of "hole scavengers" (i.e., acetate)[13] which irreversibly react with photogenerated holes.[8] Removal of electrons from recombination sites would similarly give rise to an enhanced anodic photocurrent, if the reduced form of the "electron scavenger" is oxidizable at the inert electrode. In this regard, the photodeposition of noble metals on TiO_2 particles[15,16] and single crystals[17] clearly results from reactions of surface electrons with solution species. This report describes studies of the enhancement of photocurrents derived from TiO_2 suspensions by the trapping of electrons at the surface of the semiconductor particle. Specifically, the role of Cu^{2+}, Fe^{3+}, and Pt^0 as electron-trapping agents with semiconductor electrodes is discussed.

Experimental Section

Reagent-grade TiO_2 (Matheson Coleman and Bell, MCB) was used in all experiments. The powder was confirmed to be in the anatase form by X-ray diffraction with a grain diameter of 0.2 μm by scanning electron microscopy (SEM). The suspensions were prepared by addition of 0.25 g of TiO_2 powder to 100 mL of triply distilled H_2O containing 0.02 M HNO_3 (MCB reagent grade) and in most cases 4 M acetic acid (MCB). Vigorous stirring of this mixture resulted in a finely divided TiO_2 suspension. SEM of the dried TiO_2 powder after suspension showed the same grain size as the original material. All suspensions were degassed for at least 2 h with prepurified nitrogen before photochemical experiments.

Experiments were performed in a 200-mL Pyrex H-cell, equipped with a flat optical window sufficiently large to allow illumination of the entire width of the cell. The collector electrode used was a platinum flag (20 × 20 × 0.25 mm). The counterelectrode was a large platinum flag placed in a compartment separated from the slurry compartment by a fine-porosity glass frit. A saturated calomel electrode (SCE) was used as a reference electrode; all redox potential values are reported vs. the SCE.

Cupric ion was added to the photochemical cell as either an 8 or 80 mM solution of $Cu(OAc)_2{\cdot}2H_2O$ (MCB, reagent grade). $FeCl_3{\cdot}6H_2O$ (Mallinckrodt) was also added as a dilute solution.

Studies of chemisorbed hydrogen atoms on platinum film were performed in a one-compartment cell with a flat optical window. The solvent employed was 0.02 M H_2SO_4 (MCB, reagent grade) prepared with triply distilled water. A platinum flag was used as a counterelectrode, and a saturated NaCl calomel electrode (SSCE) used as a reference electrode. Before all experiments, the platinum films were pretreated by holding the electrode at +2.0 V where rapid evolution of O_2 was observed for 5 min.

Films of TiO_2 on platinum were prepared by two methods. Vacuum evaporation of titanium onto platinum foil (10 × 10 × 0.025 cm) followed by oxidation of this electrode at 800 °C for 15 min gave a thin film of TiO_2 (rutile) ~100 nm thick. These are designated as Pt/TiO_2.

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Although these electrodes exhibited the desired behavior, they tended to degrade slowly under the experimental conditions. A different method that was employed resulted in a much sturdier and more easily studied electrode. Flat pieces of titanium (13 × 10 × 1 mm) were annealed under vacuum (10^{-4} torr) for 2 h and then heated in air for 24 h at 600 °C. Such treatment resulted in a grayish film of TiO_2 (rutile) ~400 nm thick. One side of an electrode was abrasively treated to remove the TiO_2 film, and a platinum foil of identical dimensions contacted to the exposed titanium by silver epoxy. After drying, the narrow sides of the electrode were covered with 5 min epoxy, and the electrode was allowed to cure overnight before use. Such electrodes were designated $Pt/Ti/TiO_2$.

Photocurrents and cyclic voltammograms were recorded with a Princeton Applied Research (PAR) Model 173 potentiostat/galvanostat, a PAR Model 175 Universal programmer, and a Houston Instruments Model 2000 X-Y recorder. The illumination source was a 3.0-kW Xe arc lamp (Christie Corp., Los Angeles, CA, Model VF30KK) operated at 1.6 kW.

Results

Effect of Cupric Ion. As previously reported,[10,13] irradiation of stirred TiO_2 suspensions in aqueous media (pH 2) resulted in the generation of small anodic photocurrents ($<1\ \mu A/cm^2$) as measured by the collector electrode in quiet cells; addition of acetate to the suspension was found to increase the observed photocurrent. The maximum anodic photocurrent obtained for stirred TiO_2 suspensions ($\simeq 2$ mg/mL) in the presence of acetate (4 M) with the collector electrode held at 0.5 V vs. SCE was 1.2 $\mu A/cm^2$. This current was independent of the position and orientation of the collector electrode and decreased to essentially zero if stirring was stopped. These observations illustrate that the measured current originates from charges on the bulk suspension, *not* from light impinging on the collector electrode itself.

Addition of small amounts of $Cu(OAc)_2 \cdot 2H_2O$ to stirred TiO_2 suspensions resulted in a large enhancement of the anodic photocurrent (i) produced by these cells when the collector electrode was held at +0.5 V (Figure 1). Under illumination ($h\nu > E_g$, $\lambda < 390$ nm) a steadily increasing current was observed. When the light was removed, the anodic current persisted and decayed slowly to zero. Both the rate of photocurrent increase ($\Delta i/\Delta t$) and its decay in the dark were proportional to the concentration of cupric ion, and a plot of $\Delta i/\Delta t$ vs. $(Cu^{2+})^{1/2}$ yielded a straight line (Figure 2). Under prolonged illumination the photocurrent eventually reached a maximum value, which also depended upon (Cu^{2+}). For example, when (Cu^{2+}) = 2.3 mM, the steady-state current after illumination for 100 min was 0.8 mA/cm^2. This represents a *500-fold* increase in current compared to a photocell without cupric ion. Additionally, TiO_2 suspensions irradiated in the presence of cupric ion were capable of storing this charge with the light off. When the suspensions were irradiated and then the light and the collector electrode turned off for several hours the current observed upon reconnecting the collector electrode (in the dark) was essentially the same as that observed immediately before illumination was terminated (Figure 3).

The results obtained were independent of the position of the collector electrode within the cell. Moreover, when the stirring was stopped, the observed current immediately returned to zero. These observations indicate that the enhanced photocurrents arise from *bulk* effects, not from light impinging on the collector electrode. Because these suspensions were rather opaque and light did not appear to penetrate very deeply into the cell, TiO_2 particles were probably illuminated only when they passed close to the cell window.

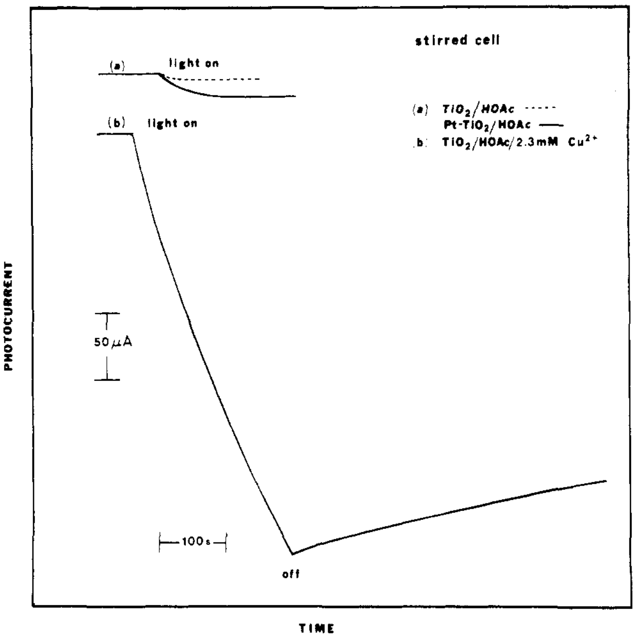

Figure 1. Photocurrent vs. time for stirred TiO_2 suspension photocells. Cell conditions: TiO_2 powder (250 mg); H_2O (110 mL); HOAc (25 mL); HNO_3 (0.02 M). Platinum collector electrode potential at +0.5 V vs. SCE. a: (– – –) TiO_2; (—) Pt/TiO_2. b: $Cu(OAc)_2 \cdot 2H_2O$, 2.3 mM.

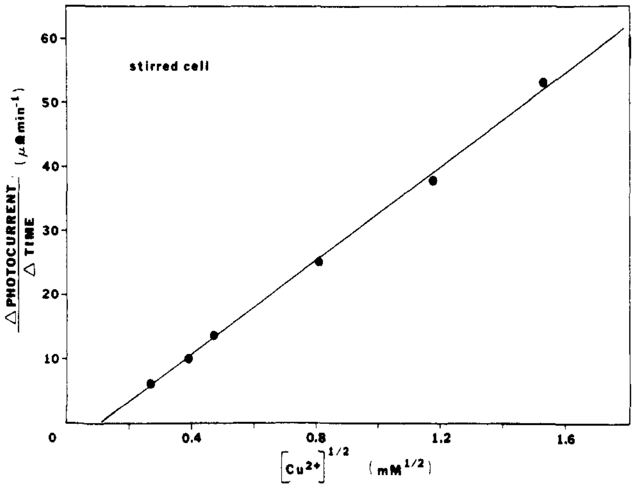

Figure 2. Dependence of rate of the change of photocurrent with time ($\Delta i/\Delta t$) with $(Cu^{2+})^{1/2}$ (added as $Cu(OAc)_2 \cdot 2H_2O$) for stirred TiO_2 suspension photocells. Cell conditions: TiO_2 powder (250 mg); H_2O (110 mL); HOAc (25 mL); HNO_3 (0.02 M). Platinum collector electrode potential, +0.5 V vs. SCE; N_2 purged.

Introduction of a gentle stream of air over the slurry resulted in an immediate decay of the observed current to zero. Thus, air must be rigorously excluded from the photocells to observe the maximum attainable photocurrents. However, the ability of the cells to generate photocurrents can be restored to 100% of their original value by vigorously bubbling N_2 through the suspensions for about 30 min.

The effect of cupric ion on TiO_2 photocurrents was also observed in quiet cells, provided the cell was allowed to settle to such a degree that light could reach the vicinity of the collector electrode. Enhanced photocurrents in the presence of $Cu(OAc)_2 \cdot 2H_2O$ compared to TiO_2 alone were also observed under these conditions but were not as large as those observed with stirred cells (Figure 4). However, information about the potential dependence of the pho-

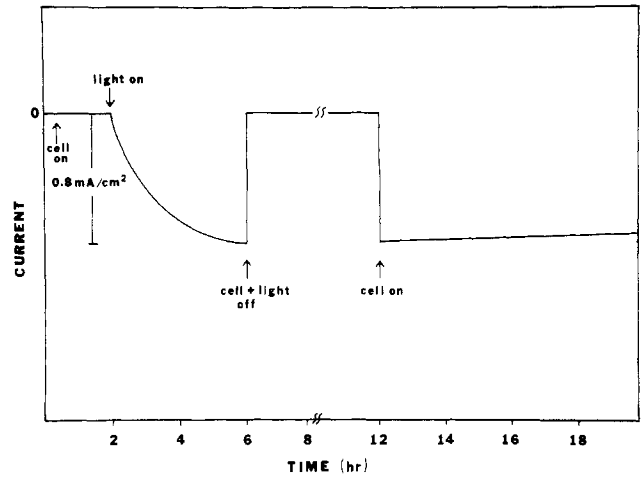

Figure 3. Current-time behavior for TiO_2 suspension photocell containing Cu^{2+} (2.3 mM). Cell conditions: TiO_2 powder (250 mg); H_2O (110 mL); HOAc (25 mL); HNO_3 (0.02 M). Platinum collector electrode potential at +0.5 V vs. SCE; N_2 purged.

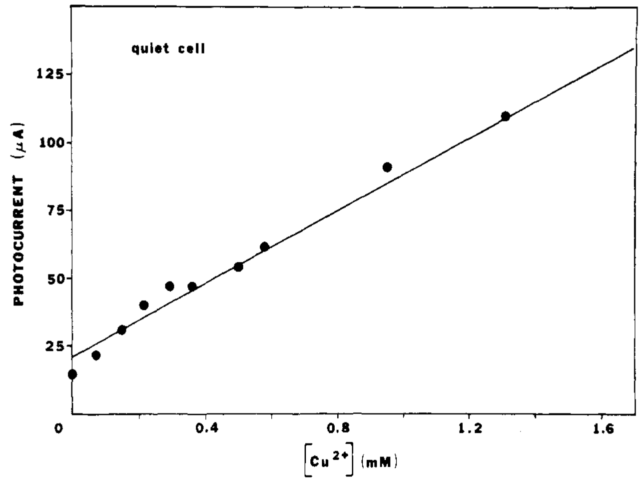

Figure 4. Dependence of photocurrent on (Cu^{2+}) for quiet TiO_2 suspension photocells. The suspension was allowed to settle for 30 min before measurements. Cell conditions: TiO_2 powder (250 mg); H_2O (110 mL); HOAc (25 mL); HNO_3 (0.02 M). Platinum collector electrode potential at +0.5 V vs. SCE; N_2 purged.

tocurrent could be obtained from such studies. Comparisons of photocurrent vs. collector electrode potential curves for TiO_2 suspensions in the presence and absence of Cu^{2+} showed a marked difference between the two systems. For TiO_2 alone (in 4 M acetic acid) the anodic photocurrent started at potentials positive of −0.4 V vs. SCE and gradually increased as the collector electrode potential became more positive (Figure 5). In the presence of Cu^{2+} (6 mM), the photocurrent generated by the cell started at ~+0.1 V and was independent of the collector electrode potential in the range +0.2 to +0.6 V. Experiments at potentials negative of +0.2 V are complicated by direct Cu^{2+} reduction at the collector electrode.

The enhancement of i by Cu^{2+} was also observed in the absence of acetate. However, the maximum attainable photocurrent for these stirred cells was much smaller (~45 $\mu A/cm^2$) than those containing acetate (4 M) at the same (Cu^{2+}) (2.3 mM). Additionally, the rate of photocurrent increase, $\Delta i/\Delta t$, showed *no* dependence on (Cu^{2+}) in the range studied, 0.05–1.0 mM, in the absence of acetate.

The results with cupric ion, which are discussed in more detail below, can be explained by the more efficient capture of electrons by Cu^{2+} producing Cu^0 which is oxidized at the collector electrode. A question of interest is whether a good oxidant, such as Fe^{3+}, which produces a soluble reduced form would be equally effective in increasing the anodic photocurrent with these suspensions.

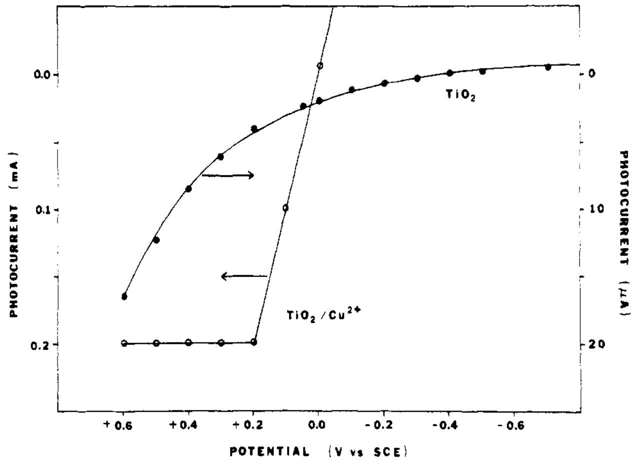

Figure 5. Dependence of photocurrent on collector electrode potential for quiet TiO_2 suspension photocells in the absence (upper curve, right ordinate) and presence (lower curve, left ordinate) of 2.3 mM Cu^{2+}. Cell conditions: TiO_2 powder (250 mg); H_2O (110 mL); HOAc (25 mL); HNO_3 (0.02 M). N_2 purged.

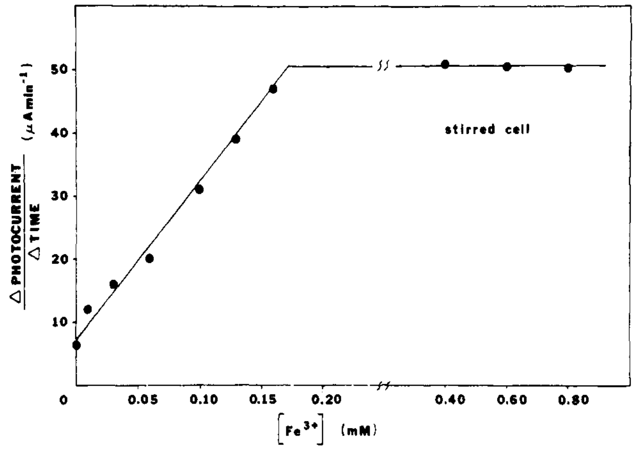

Figure 6. Dependence of $\Delta i/\Delta t$ on (Fe^{3+}) for stirred TiO_2 suspension photocells. Cell conditions: TiO_2 powder (250 mg); H_2O (110 mL); HOAc (25 mL); HNO_3 (0.02 M). Platinum collector electrode potential at +0.6 V vs. SCE; $Fe^{3+} \simeq FeCl_3{\cdot}6H_2O$; N_2 purged.

Effect of Ferric Ion. Addition of $FeCl_3{\cdot}6H_2O$ to the TiO_2 suspension also resulted in a dramatic increase in the photocurrent produced with these cells with the collector electrode held at +0.6 V. The rate of photocurrent increase, $\Delta i/\Delta t$, was much greater for smaller concentrations of Fe^{3+} compared to that observed for cells containing cupric ion. Thus, $\Delta i/\Delta t$ linearly increased with (Fe^{3+}) to 40 μA/min at 0.2 mM Fe^{3+}, whereas with Cu^{2+}, $\Delta i/\Delta t$ = 10 μA/min at this concentration. Although the photocurrent increased more rapidly with concentration for Fe^{3+} compared to Cu^{2+}, the maximum photocurrent that could be attained from TiO_2 suspensions containing either ion was identical. As shown in Figure 6, when (Fe^{3+}) was >0.2 mM, $\Delta i/\Delta t$ was constant at a value which was nearly identical with that observed for cells containing Cu^{2+}. Additionally, when (Fe^{3+}) = 2.3 mM, the maximum photocurrent that could be realized was also 0.8 mA/cm^2. Illumination of a suspension containing 2.3 mM Fe^{3+} and 4 M acetic acid for 12 h resulted in complete loss of the initial orange color of the solution (attributable to Fe^{3+}, as verified by visible spectroscopy) to yield an essentially colorless solution. Filtration of this suspension gave a colorless filtrate. When this filtrate was re-added to the cell, the measured dark current was identical with that

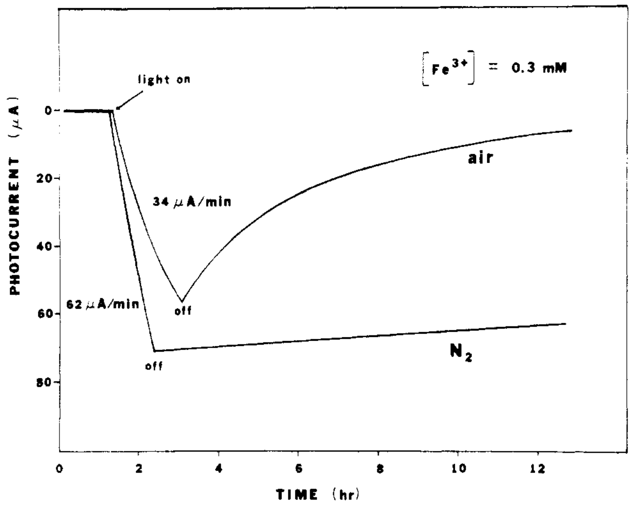

Figure 7. Photocurrent vs. time for stirred TiO_2 suspension photocells containing 0.3 mM Fe^{3+} in the presence (upper curve) and absence (lower curve) of air. Cell conditions: TiO_2 powder (250 mg); H_2O (110 mL); HOAc (25 mL); HNO_3 (0.02 M). Platinum collector electrode potential at +0.6 V vs. SCE; $Fe^{3+} \simeq FeCl_3{\cdot}6H_2O$.

recorded before filtration. This current decayed in the dark normally, concomitant with the reappearance of the orange Fe^{3+} ion. These results suggest that Fe^{3+} is reduced to Fe^{2+} during irradiation of these suspensions. The most marked difference between the experiments with Cu^{2+} and Fe^{3+} is the greatly decreased sensitivity of the photocurrents from cells containing Fe^{3+} toward oxygen. Admission of copious amounts of air to the cell after illumination showed no effect on the rate of current decay. Additionally, the photocurrent enhancement by Fe^{3+} was still evident in cells which were saturated with air before illumination, although the rate of photocurrent increase was smaller with these cells (Figure 7).

The utilization of more noble transition-metal redox couples in TiO_2 suspensions did not lead to enhancement of the photocurrents. Addition of $PdCl_2$ or H_2PtCl_6 to TiO_2 suspensions resulted in irreversible Pd^0 or Pt^0 deposition on the particles; no anodic current was observed when the collector electrode was held positive of the Pd/Pd^{2+} or Pt/Pt^{4+} redox couples (E_{redox} = +0.59 and +0.49 V, respectively). Presumably, it is difficult to oxidize these deposits for the same reason that electrodes of these materials do not dissolve at potentials positive of their redox potentials. Other processes (i.e., oxide film formation) preclude direct oxidation of the metal.

Adsorbed Hydrogen at Pt/TiO₂. The observation that platinized TiO_2 particles generated larger photocurrents compared to untreated TiO_2 in the presence of acetate (Figure 1) suggested that Pt also participates in capture of the photogenerated electron. To gain insight into the electrochemical reactions that may take place at the platinum sites of these particles, we undertook an investigation of the electrochemical behavior of platinum surfaces contacted to TiO_2 films. The electrodes were constructed in such a manner that the TiO_2 film could be illuminated and the platinum surface on the dark side monitored electrochemically, e.g., by voltammetric experiments (see Experimental Section). The contact between the TiO_2 film and the titanium surface (which was contacted to platinum) was ohmic in nature.[18]

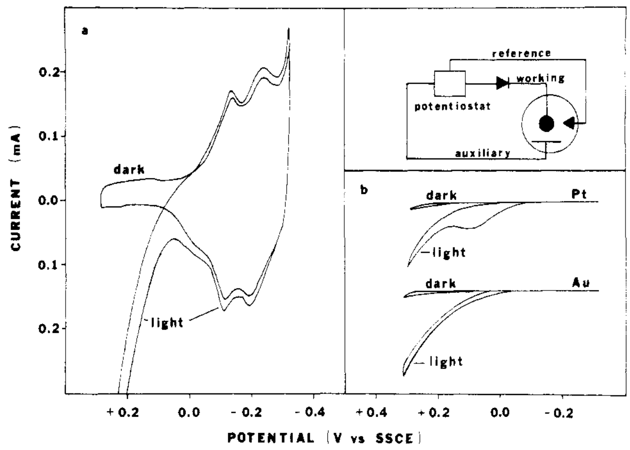

Figure 8. Current vs. potential curves for the platinum film of the $Pt/Ti/TiO_2$ electrode immersed in 0.02 M H_2SO_4. (a) Voltammogram recorded without diode in place. (b) Voltammogram recorded with diode between the potentiostat and the $Pt/Ti/TiO_2$ electrode. The lower voltammogram was recorded for an $Au/Ti/TiO_2$ electrode under identical conditions.

The electrochemical behavior of platinum electrodes in aqueous media is well documented,[19-21] and voltammetric waves associated with reduction and oxidation of adsorbed hydrogen species are observed. The idea of this experiment was to compare the voltammetric behavior of the Pt/TiO_2 electrode under or after illumination with that of bare Pt to see whether reduced intermediates at the Pt (e.g., adsorbed hydrogen) could be detected electrochemically. When the platinum electrode immersed in a solution of 0.02 M H_2SO_4 was scanned in the dark between +0.3 and −0.3 V, the familiar waves for the formation and oxidation of adsorbed hydrogen (Pt–H) appeared (Figure 8a). Thus, oxidation peaks in this potential region can be used to identify submonolayer amounts of Pt–H. To prevent the electrochemical generation of Pt–H during illumination with the Pt held at potentials negative to where Pt–H is oxidized, a signal diode (IN69A, R_b/R_f = 167) was inserted into the working electrode lead between the cell and the potentiostat (see insert, Figure 8) in such a direction that only anodic current could pass. Thus, a cyclic voltammogram of the Pt/TiO_2 electrode for a scan between +0.3 and −0.3 V showed essentially a flat base line (Figure 8b). Upon illumination of the TiO_2 film, no reduction current was observed, but on the anodic sweep a wave centered at ~0.1 V appeared. The wave was rather broad, suggesting the presence of more than one peak. A peak at an identical potential with identical shape could be produced by holding the Pt at −0.3 V in the dark for several seconds *without* the diode in place, followed by insertion of the diode and scanning in the anodic direction. This observation suggests that the wave is due to poorly resolved peaks associated with oxidation of Pt–H species. The shift to more positive potentials with the diode in place is consistent with the voltage drop observed for germanium diodes of this type. When similar experiments were performed with a gold film contacted ohmically to TiO_2, this effect was not observed. These results can be explained by the production of adsorbed hydrogen by electrons photogenerated in the TiO_2 which move to the Pt where proton reduction occurs.

The effect of illumination upon scanning the potential of the Pt/TiO_2 without the diode was also interesting and provided evidence for an additional effect. The dark scan for this electrode showed peaks at +0.40, −0.12, and −0.24 V vs. SCE, the former ascribed to Pt–O reduction and the

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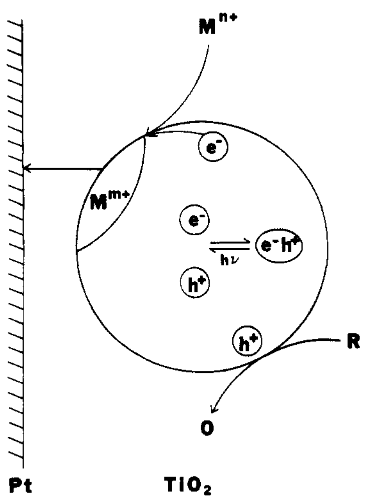

Figure 9. Schematic representation of the particles and collector electrode reactions occurring in TiO_2 suspension of photocells. (In the case of Cu, M^{m+} is deposited on the particle; for Fe, M^{m+} is likely to be soluble in the cell medium.) R $\simeq$ acetate; O $\simeq$ CH_4, C_2H_6, CO_2.

latter two to Pt–H formation (by reduction of proton). Upon sweeping in the anodic direction, oxidation of the Pt–H species is observed. Illumination of the TiO_2 film, however, had a marked effect on the voltammogram. As expected, large photocurrents generated by the TiO_2 film were observed at potentials of >0.0 V. However, increases in the height of both the *cathodic* and anodic peaks ascribed to Pt–H species were also observed. The increase in cathodic current can be ascribed to sub-band-gap photocurrent, which is believed to result from the reduction of surface states.[22-24] Increased anodic currents were also observed upon sweeping in the anodic direction. We have verified this sub-band-gap photocurrent on polycrystalline TiO_2 electrodes (with Ga/In contacts) and have found the magnitude of these currents in the Pt–H region to be similar to the increase in the cathodic and anodic peak heights. Additionally, it was observed that the current increase under illumination decreases with increasingly negative cathodic return potentials, consistent with behavior expected for surface-state phenomena.

Discussion

Semiconductor particles such as TiO_2 behave as short-circuited photoelectrochemical cells, where both cathodic and anodic reactions occur on the same particle. In these experiments, anodic photocurrent from illuminated TiO_2 suspensions arises via transfer of photogenerated electrons trapped on the particle itself, from reduced species on the particle surface (e.g., Cu) or from photogenerated reductants in solution (e.g., Fe^{2+}). The anodic currents that result from electrons trapped on the particle (e.g., as Ti^{3+} centers) are rather small, probably because the buildup of electronic charge on the particle increases the rate of electron–hole (e^-h^+) recombination. In this case the role of the Cu^{2+} and Fe^{3+} is the removal of electrons from e^-h^+ recombination sites with the production of oxidizable species. These reductions can occur, since the measured potential of the photoelectrons in the TiO_2 (−0.4 V vs. SCE), as determined from the potential for the onset of anodic photocurrent, is negative of the redox potentials for both the Cu^{2+}/Cu (+0.10 V) and the Fe^{3+}/Fe^{2+} (+0.53 V) couples. The reduced form is then oxidized at the collector electrode, which is held at a potential positive of the redox potential of the couple (Figure 9). The steady-state anodic currents observed at the applied potential were mass-transfer limited; i.e., application of more positive potentials did not increase the observed current. This is clearly shown for Cu^{2+} in Figure 5. The process can be represented by Scheme I. This scheme assumes

Scheme I

$$TiO_2 + h\nu \rightarrow TiO_2\ (e^-h^+) \qquad (1)$$

$$TiO_2\ (e^-h^+) + \text{Red} \rightarrow TiO_2\ (e^-) + \text{Ox} \qquad \text{(hole reaction)} \quad (2)$$

$$TiO_2\ (e^-h^+) \rightarrow TiO_2 \qquad \text{(recombination)} \quad (3)$$

$$2TiO_2\ (e^-) + Cu^{2+} \rightarrow 2TiO_2 + Cu^0 \qquad \text{(electron trapping)} \quad (4)$$

or

$$TiO_2\ (e^-) + Fe^{3+} \rightarrow TiO_2 + Fe^{2+} \qquad \text{(electron trapping)} \quad (5)$$

$$Cu \rightarrow Cu^{2+} + 2e \qquad \text{(at collector electrodes)} \quad (6)$$

or

$$Fe^{2+} \rightarrow Fe^{3+} + e^- \qquad \text{(at collector electrode)} \quad (7)$$

that reaction of the hole with acetate or a reductant is rapid and the anodic current is governed by the rate at which electrons are trapped. This assumption, rather than the alternative where electron trapping is more rapid, is consistent with the experimental finding that acetate is oxidized at illuminated TiO_2 particles,[8] that acetate oxidation is nearly 3000 times faster than Cu^{2+} reduction,[29] and that TiO_2 particles can store negative charge for substantial periods of time.[15]

Photocurrent Enhancement by Cu^{2+}. The proposal that Cu^{2+} is reduced to Cu^0 on the surface of an illuminated TiO_2 particle in these cells is supported by the previous observation that significant deposits of Cu^0 are observed when TiO_2 is illuminated in the presence of Cu^{2+}.[15] Similar results were obtained for n-TiO_2 single crystals.[15,18] In related experiments, we have found that illumination of polycrystalline TiO_2 (rutile) electrodes in aqueous Cu(II) solutions (with acetate) led to copper deposition primarily on the dark side of the electrode. Lesser deposits were observed on the illuminated side, but only on locations which were obvious defects (scratches, holes, etc.) in the TiO_2 film. This behavior suggests the possibility that the extent of *net* Cu^{2+} reduction on an illuminated surface of a particle is minimal and that *net* Cu^0 deposition occurs on a dark side of the particle. This may occur since the larger concentration of holes on the illuminated side of the particle will rapidly oxidize Cu^0 species. Such a process was previously suggested[15] by the observations that illumination of a surface of an n-TiO_2 single crystal with Cu^0 deposits resulted in removal of these species via hole oxidation to Cu^{2+}. However, since the dimensions of these

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particles are small, light probably penetrates completely through the particle. For example, if the absorptivity is 5×10^4 cm^{-1}, 37% of the light will emerge from the "dark side" of a 2000-Å-diameter particle. Moreover, it may not be proper to discuss the behavior of the particles in terms generally used for single-crystal semiconductors where an electric field at the interface promotes e^-h^+ separation. The thickness of the space charge region at the semiconductor/solution interface, W, is given by

$$W \simeq (1.05 \times 10^3)(\epsilon \Delta V / N_D)^{1/2} \text{ cm} \qquad (8)$$

where ϵ is the dielectric constant, ΔV is the potential drop (V), and N_D is the dopant density (cm^{-3}). With $\epsilon = 10$, $\Delta V = 0.1$ V, and $N_D = 10^{15}$ cm^{-3}, $W \simeq 3320$ Å. Thus, for a 2000-Å particle surrounded by liquid, the existence of an appreciable field between the semiconductor surfaces appears unlikely. Thus, it may be more appropriate to consider the very large surface area of these particles with respect to total volume and describe the process in molecular terms. For example, one can consider the e^-h^+ formation as a L → M charge transfer, with subsequent reduction of the participating ion as an inner-sphere charge-transfer reaction.[25,26] The e^-h^+ pair can be envisaged as a localized e^- (a Ti(III) site),[27] and the hole residing on an oxygen atom (or as a hydroxyl species),[9,28] so that electron transfer can occur via a Ti(III)–O–M^{n+} intermediate (the bonding oxygen atoms need not be the same one on which the hole resides). The electron-transfer behavior of Ti(III) has been well documented[30-37] and is consistent with such a scheme. It should be noted that facile electron transfer from Ti(III) to Co(III) was observed for carboxylato complexes of the latter;[38] thus, acetate may play an important role in this regard. It is also possible that adsorbed ions on the particle surface (e.g., OH^-) produce a local electric field which promotes charge separation.

Since the Cu^+ ion is not very stable in the medium employed in these cells, we favor a scheme in which Cu^0 on the TiO_2 particle surface is oxidized at the collector electrode. However, the intermediacy of Cu^+ ion cannot be unambiguously discounted, especially in light of the observation that the rate of photocurrent increase, $\Delta i/\Delta t$, varies linearly with $(Cu^{2+})^{1/2}$. This suggests that one-electron reduction to Cu^+, followed by rapid disproportionation, is plausible (Scheme II). Addition of KCl to the suspensions resulted in a marked decrease in the observed photocurrent. Since chloride ion is known to stabilize Cu(I) by complexation and decrease the extent of Cu^0 formation, this behavior suggests that Cu^0 is the species responsible for the observed enhancement of photocurrent. The inability of Cu(I) species to enhance the photocurrent may be due to a "short-circuiting" of the particle by Cu(I) (i.e., Cu(I) + $h^+ \rightarrow Cu^{2+}$), which does not significantly occur for Cu^0 or Fe^{2+}. This is consistent with the greater ease of oxidation associated with Cu(I) ($E_{redox}(Cu^{2+}/Cu^+) = -0.084$ V). The Cu^0 species are readily oxidized at the collector electrode which is biased positive of the Cu^{2+}/Cu^0 couple. The observation that the anodic photocurrent in quiet cells was independent of the collector electrode potential when it was positive of the redox potential of the Cu^{2+}/Cu^0 couple supports this claim.

Scheme II

$$Cu^{2+} + e^- \rightleftarrows Cu^+ \qquad (9)$$

$$2Cu^+ \rightleftarrows Cu^{2+} + Cu^0 \qquad K_{eq} \simeq 10^6 \qquad (10)$$

The importance of an efficient hole scavenger is illustrated by the significantly larger photocurrents observed when acetate was present. Efficient removal of the photogenerated holes from the particle prevents deleterious oxidation of Cu^0 species, and e^-h^+ recombination, thus allowing *net* reduction of Cu^{2+}. The products of acetate oxidation (CH_4, C_2H_6, H_2, and CO_2) do not back-react with Cu^0, whereas O_2 produced by H_2O oxidation possesses this capability. The observation that the photocurrent is independent of (Cu^{2+}) when only H_2O is present as a hole scavenger suggests that this process is slow and that the availability of electrons for Cu^{2+} reduction is limited by significant electron–hole recombination.

The observation that the anodic current generated by these cells decays rapidly to zero upon introduction of air is consistent with reduction of O_2 by photogenerated electrons,[27] preventing Cu^0 formation, and by finely divided Cu^0 on the particle surface. At this time, however, we have not established whether the reduction product is H_2O_2 ($E_{redox} = 0.32$ V) or H_2O ($E_{redox} = 0.94$ V).

The observation of photocurrent enhancement by cupric ion is interesting in light of recent reports which show the presence of cupric ion to enhance markedly the oxidation of organic substrates via photogenerated holes from TiO_2 powders. For example, the oxidation of *N*-acetylpyrrolidine was effected by illuminated TiO_2 powders concomitant with Cu^0 deposition.[5] Also, increased yields of photocatalytic oxidation of aromatic compounds in the presence of Cu^{2+} were reported.[3]

Photocurrent Enhancement by Fe^{3+}. The observation of photocurrent enhancement by Fe^{3+} is consistent with the suggested fast reaction of this species with photogenerated electrons on TiO_2 particles.[3] In this case, the low yields of aromatic oxidation products with TiO_2 suspensions containing Fe^{2+} were attributed to a short-circuiting mechanism (Scheme III). However, our experiments illustrate that acetate oxidation proceeds much faster than Fe^{2+} oxidation. The observation that experiments in the absence of acetate produced much smaller photocurrents ($i_{max} \sim 40$ μA/cm^2 at $(Fe^{3+}) = 2.3$ mM) supports this claim. Under these conditions, oxidation of Fe^{2+} by photogenerated holes can become more significant as the rate of H_2O oxidation is slow compared to that of acetate.[29] The observation that Fe^{2+} oxidation is much slower than acetate oxidation agrees with previous reports of similar rates of oxidation for Fe^{2+} and H_2O by photogenerated holes at TiO_2.[39,40]

Scheme III

$$h^+(TiO_2) + Fe^{2+} \rightarrow Fe^{3+} \qquad (11)$$

$$Fe^{3+} + e^-(TiO_2) \rightarrow Fe^{2+} \qquad (12)$$

The results suggest that electron trapping by Fe^{3+} proceeds more efficiently than that observed for Cu^{2+} up to the saturation limit. The presence of this limit, which is identical for either ion, suggests a limiting rate for the generation of available electrons at the TiO_2 particle surface, which in turn sets an upper limit on the photo-

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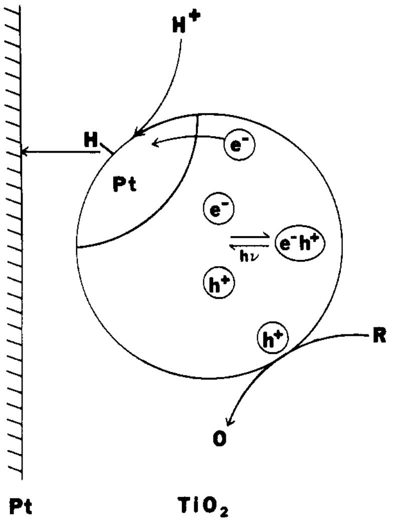

Figure 10. Schematic representation of the particle and collector electrode reactions occurring in platinized TiO_2 suspension photocells. The intermediacy of Pt–H species is illustrated. R $\simeq$ acetate; O $\simeq$ CH_4, C_2H_6, CO_2.

current that can be achieved from these suspensions. Presumably, electron–hole recombination is significant at this limit. The greater efficiency observed for experiments with Fe^{3+} may be due to the ability of the Fe^{2+} ion to migrate away from the particle into solution (thereby preventing the deleterious back-reaction) whereas Cu^0 species are probably immobilized on the particle. The greatest difference between cells containing Fe^{3+} and Cu^{2+} is the ability of the former to enhance the photocurrent in the presence of O_2. The observation that substantial photocurrents are observed in cells saturated with air suggests that Fe^{3+} competes effectively with O_2 for conduction band electrons under these conditions and the reaction of O_2 with Fe^{2+} is slow.

Electron Trapping as Pt–H Species. It was reported earlier that platinized TiO_2 particles gave rise to smaller anodic photocurrents compared to untreated TiO_2 in cells of this type; facile reduction of proton to hydrogen gas on platinum sites which was tantamount to efficient removal of electrons from the particle was proposed. However, we have now found that platinized TiO_2 gives rise to larger photocurrents in the presence of acetate than those observed on untreated TiO_2, and, on the basis of our results, we believe that this is a direct result of "electron trapping" by a proton on the platinum sites. That is, chemisorbed hydrogen is formed and serves to decrease the rate of e^-h^+ recombination. These species are then oxidized at the working electrode to give anodic photocurrent (Figure 10). The observation that these species were generated photochemically under conditions where electrochemical generation was excluded supports this proposal. On the basis of the potential value found for the onset of photocurrent for TiO_2 suspensions under these conditions (V_{onset} = –0.40 V) and $E_{1/2}$ for the oxidation of Pt–H species (–0.14 and –0.24 V), formation of the latter should be favorable. Apparently, the lifetime of these intermediates is sufficiently long and their concentration sufficiently larger that their oxidation at the collector electrode is measurable. The observation that gold and platinum foil on TiO_2 electrodes show much different behavior upon illumination, although both are in ohmic contact with the TiO_2 film, supports the claim that Pt–H species are responsible for the observed behavior. The electrochemical generation of Au–H species is not observed under these conditions, in agreement with the known behavior of gold films.[19]

Conclusions

We have demonstrated that markedly enhanced photocurrents can be obtained from illuminated TiO_2 suspensions if the cells are modified in such a manner that photogenerated electrons can be trapped, thus preventing deleterious e^-h^+ recombination. The observation of this behavior is consistent with the generation of e^-h^+ pairs upon illumination, with hole scavenging by oxidizable substrates in the cell, and reduction of either Cu^{2+}, Fe^{3+}, or H^+ (on Pt/TiO_2 particles) by photogenerated electrons at the surface of the particle. Since the space charge layer thickness for undoped TiO_2 is probably >1000 Å, and the grain size of the TiO_2 powder described above is <2000 Å, efficient separation of e^-h^+ pairs by a space charge region is unlikely. Therefore, electron traps, such as those described above, coupled with an efficient hole scavenger, may be necessary for efficient e^-h^+ separation and generation of significant amounts of photocurrent for TiO_2 suspensions. The efficiency and long-lived nature of Cu^0 deposits as electron traps is especially demonstrated by the ability of these cells to store negative charge for long periods of time; these cells might thus be useful as photoregenerative storage batteries. These results also suggest that the Cu^{2+} enhanced oxidation of organic substrates at TiO_2 powders can be attributed to the decreased rate of e^-h^+ recombination compared to systems where Cu^{2+} is absent.

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