

Photoelectrochemical Investigation on Electron Transfer Mediating Behaviors of Polyoxometalate in UV-Illuminated Suspensions of TiO₂ and Pt/TiO₂

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The role of electron acceptors in semiconductor photocatalysis is critical in determining the overall photoefficiencies, kinetics, and mechanisms. Polyoxometalates (POMs) are efficient electron acceptors and carriers in TiO₂ photocatalysis. The electron transfer mediating behaviors of a POM (PW₁₂O₄₀³⁻/PW₁₂O₄₀⁴⁻) couple were investigated photoelectrochemically in the UV-illuminated TiO₂ or Pt/TiO₂ suspensions and compared with those of an Fe³⁺/Fe²⁺ couple. POMs successfully transfer CB (conduction band) electrons on TiO₂ particles to an inert collector electrode with generating photocurrents under UV illumination. The magnitude of photocurrent is directly proportional to the reduced POM concentration ([POM⁻]) and markedly decreases in the presence of dissolved O₂ due to the rapid reoxidation of the reduced POMs by O₂. Electron donors are essential in inducing photocurrents, which are negligibly small in the absence of them. The photocurrent generation also depends on the kind of electron donors. Whereas formate as an electron donor is more efficient than acetate in generating photocurrents in the POM + TiO₂ suspension, it is far less efficient in the Fe³⁺ + TiO₂ system on the contrary. On the other hand, the platinization of the TiO₂ surface significantly affects the current collection efficiency. The POM-mediated electron transfer to the collector electrode is reduced in the Pt/TiO₂ suspension as compared with the naked TiO₂ suspension, whereas the Fe³⁺-mediated current is higher in the Pt/TiO₂ than in the naked TiO₂ suspension. The reoxidation rate of the reduced POM is accelerated on Pt surface with reducing the efficiency of current collection. Although POMs are less efficient than Fe³⁺ ions in mediating the photocurrent generation in general, they exhibit unique behaviors that are different from those of Fe³⁺.

Introduction

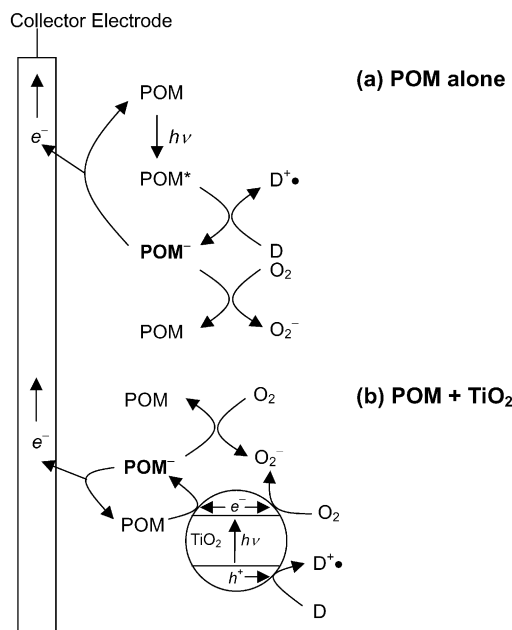
Homogeneous and heterogeneous photocatalysis plays a central role in many photochemical conversion processes, where a series of photoinduced electron transfer reactions take place upon absorbing light. Semiconductor materials have been widely investigated as a heterogeneous photocatalyst among which TiO₂ is the most popular especially for the complete oxidation of toxic contaminants in the liquid or gas phase.^{1–7} On the other hand, polyoxometalates (POMs) have been studied as a homogeneous photocatalyst^{8–11} or a heterogenized homogeneous photocatalyst¹² also for the oxidative degradation of pollutants. POMs and semiconductor photocatalysts share the same general photochemical mechanisms in their operation. Photoexcited POMs carry a strong oxidation power to directly abstract an electron from substrates or to generate OH radicals through water oxidation as the band-gap excited TiO₂ does. A homogeneous POM photocatalyst, PW₁₂O₄₀³⁻, with a band-gap energy of 3.5 eV is very similar to the heterogeneous TiO₂ photocatalyst in its light absorption and electrochemical band-edge positions.^{13,14}

Recently, the ability of PW₁₂O₄₀³⁻ as an electron acceptor has been applied to TiO₂ photocatalytic systems to enhance the rate of conduction band (CB) electron transfer and consequently to retard the fast charge-pair recombination.^{15,16} The role of electron acceptors in TiO₂ photocatalysis is critical in enhancing the overall photoefficiency. Although dissolved oxygen mol-

ecules serve as electron acceptors in most heterogeneous photocatalytic reactions, the presence of better electron acceptors is desired for higher efficiencies. Since the standard one electron reduction potential of O₂, PW₁₂O₄₀³⁻, and PW₁₂O₄₀⁴⁻ is -0.33, +0.22, and -0.025 V (vs NHE), respectively, the POM is thermodynamically a better electron acceptor than O₂. An enhanced degradation of organic compounds in the UV/TiO₂ process could be achieved in the presence of POMs.¹⁶ The reduced POMs (PW₁₂O₄₀⁴⁻ and PW₁₂O₄₀⁵⁻) that are generated upon accepting one or two CB electrons on TiO₂ are relatively stable, absorb visible light (λ_{max} = 650 and 751 nm), and are readily reoxidized to PW₁₂O₄₀³⁻ by transferring electrons to oxidants (electron acceptors) such as O₂.¹⁴ In this case, POM acts as an electron transfer mediator (or electron shuttle) between TiO₂ particles and the final electron acceptors (dioxygen) with enhancing the overall photoefficiency.

This paper describes a photoelectrochemical study on POMs as a reversible electron shuttle. The electron shuttling behaviors of the PW₁₂O₄₀³⁻/PW₁₂O₄₀⁴⁻ redox couple in an aqueous solution or TiO₂ suspension can be investigated by monitoring photocurrents collected on an inert electrode as illustrated in Scheme 1. The POM redox couple efficiently mediates the electron transfer from the TiO₂ CB to the collector electrode. The photocurrent generation is directly proportional to the POM⁻ concentration and is sensitively affected by other experimental parameters such as electron donors, dissolved oxygen, and the surface modification of TiO₂. The electron shuttling behaviors of the POM couple are compared with those

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SCHEME 1: POM-Mediated Electron Collection on an Inert Electrode^a


^a (a) Direct electron transfer from POM in UV-illuminated aqueous solution. (b) POM as an electron shuttle in UV-illuminated TiO₂ suspension. D represents an electron donor, which is formate or acetate in this study.

of the Fe³⁺/Fe²⁺ redox couple, and their implications for photocatalytic systems are discussed.

Experimental Section

Materials and Reagents. TiO₂ powder (Degussa P25), a mixture of anatase and rutile (8:2), was used as received as a heterogeneous photocatalyst. Although the presence of two crystalline phases with slightly different CB positions might exhibit mixed electron transfer behaviors, this commercial TiO₂ is selected in this study for its wide popularity as a photocatalyst and plenty of published data on its photocatalytic behaviors. HNa₂PW₁₂O₄₀ (Riedel-de Haën) of reagent grade was used as a homogeneous POM photocatalyst. Sodium formate (>99%, Acros), sodium acetate (Merck), FeCl₃·6H₂O (>99%, Kanto), and H₂PtCl₆·6H₂O (Aldrich) were used as received.

Preparation of Pt/TiO₂ Photocatalyst. Platinized TiO₂ was prepared using a photodeposition method as reported previously.^{17,18} An aqueous TiO₂ suspension (0.5 g/L) containing 1 M methanol and 1 × 10⁻⁴ M chloroplatinic acid (H₂PtCl₆) was irradiated with a 200-W medium pressure mercury lamp for 30 min. After irradiation, the suspension was filtered with a 0.45 μm filter, washed with distilled water, and collected as powder after drying at 70 °C. A typical Pt loading on TiO₂ was estimated to be ca. 0.2 wt % by comparing the chloroplatinate concentrations in solution before and after the photodeposition.

Photoelectrochemical Test. Photoelectrochemical measurements were carried out in a 100-mL glass reactor with a Pyrex window (5 cm in diameter) for UV illumination. In this reactor, TiO₂ (or Pt/TiO₂) and other necessary electron donors or acceptors were mixed in distilled water, and the suspension pH was adjusted to 1.95 ± 0.05 with HClO₄. A platinum plate (1 × 1 cm², 0.125 mm thick, both sides exposed to the solution, Aldrich), a saturated calomel electrode (SCE), and a platinum gauze were immersed in the reactor as a working (collector), reference, and counter electrode, respectively. Nitrogen gas (>99.9%) was continuously purged through the suspension

TABLE 1: Elementary Reaction Steps in the Process of Electron Collection on an Inert Electrode (Scheme 1) through Redox Mediator Couples (POM/POM⁻ and Fe³⁺/Fe²⁺)

T1	POM + <i>hν</i> → POM*
T2	POM* → POM
T3	POM* + D → POM ⁻ + D ⁺
T4	POM ⁻ + O ₂ → POM + O ₂ ⁻
T5	POM ⁻ + H ⁺ → POM + 1/2H ₂
T6	TiO ₂ + <i>hν</i> → e _{cb} ⁻ + h _{vb} ⁺
T7	h _{vb} ⁺ + D → D ⁺
T8	POM + e _{cb} ⁻ → POM ⁻
T9	O ₂ + e _{cb} ⁻ → O ₂ ⁻
T10	Fe ³⁺ + e _{cb} ⁻ → Fe ²⁺
T11	Fe ²⁺ + O ₂ → Fe ³⁺ + O ₂ ⁻
T12	POM ⁻ → POM + e ⁻ (POM-mediated I)
T13	Fe ²⁺ → Fe ³⁺ + e ⁻ (Fe ³⁺ -mediated I)
T14	TiO ₂ (e _{cb} ⁻) → e ⁻ (negligibly small)

when the absence of dissolved oxygen was required. Photocurrents in the suspension were measured by applying a potential (+0.6 V vs SCE) to the Pt working electrode using a potentiostat (EG&G 263A2) connected to a computer. A 30-W black light lamp (ca. 130 μW/cm² for 300 < λ < 400 nm) was a UV light source. Assuming the wavelength of incident photons to be 365 nm, the total photon flux into the reactor is calculated to be 4.7 × 10¹⁵ photons/s. During the photoelectrochemical measurements, the suspension was magnetically stirred. A UV-vis spectrophotometer (Shimadzu UVPC-2401) was used to measure the concentrations of photoreduced POM by monitoring its absorbance at λ = 751 nm (ε₇₅₁ = 2 × 10³ M⁻¹ cm⁻¹).¹⁰

Results and Discussion

POM Mediated Photocurrent Generation. PW₁₂O₄₀³⁻ is a homogeneous photocatalyst that is excited by absorbing UV and subsequently induces electron transfer reactions.⁹ Excited *PW₁₂O₄₀³⁻ can abstract one electron from an electron donor to be reduced to PW₁₂O₄₀⁴⁻, which comes back to an oxidized form either by releasing an electron at the collector electrode or by transferring an electron to electron acceptors such as O₂ as shown in Scheme 1. Collected electrons come either directly from the reduced PW₁₂O₄₀⁴⁻ (Scheme 1a) or indirectly from TiO₂ CB through PW₁₂O₄₀⁴⁻ (Scheme 1b). The presence of dissolved oxygen reduces the efficiency of current collection in any case. Table 1 lists the elementary reaction steps in this electron collection process.

Figure 1a compares the time profiles of collected current densities, *I* (μA cm⁻²), with varying concentrations of PW₁₂O₄₀³⁻ when UV is illuminated to an aqueous solution of PW₁₂O₄₀³⁻ and formate (the case of Scheme 1a). In the absence of dissolved oxygen, the currents slowly increase and get saturated within 4 h of illumination. With [POM] = 1.0 mM, the saturated current density of about 40 μA cm⁻² corresponds to the apparent photonic efficiency of current collection [ϕ = (number of electrons collected)/(number of incident photons)] of 11% or so. This number should be taken as a lower limit because the scattered light intensity is not taken into account. On the other hand, in the presence of oxygen (open to air), the current collection was negligible, which indicates that the reoxidation of POM⁻ by O₂ (reaction T4) is much faster than the electron collection on the Pt electrode (reaction T12). The photocurrents generated in the POM only solution (without formate) were very small (<1 μA cm⁻²), which reflects that the presence of electron donors is essential for an efficient electron collection at the electrode. The collected photoinduced current density, Δ*I*, is directly proportional to [POM⁻], not to [POM]₀ as shown in Figure 1b. The photoreduction of POM was visibly detected

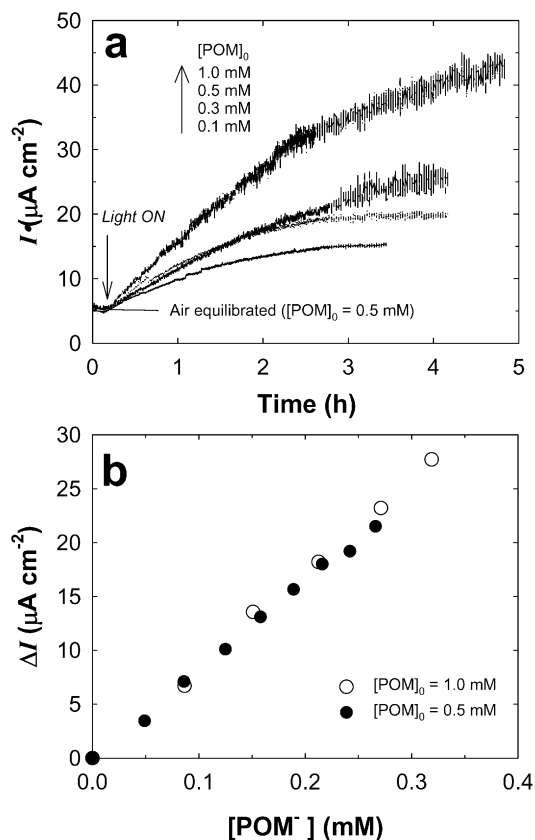


Figure 1. (a) POM-mediated photocurrent generation in aqueous solutions with varying concentrations of $\text{PW}_{12}\text{O}_{40}^{3-}$. (b) Plot of photoinduced currents, ΔI ($\Delta I = I_{\text{light}} - I_{\text{dark}}$), vs $[\text{POM}^-]$ (estimated from A_{751}). Experimental conditions were the following: $[\text{formate}]_0 = 0.2$ M; $\text{pH}_i = 1.95 \pm 0.05$; platinum collector electrode held at +0.6 V (vs. SCE); illuminated with 30 W black lamp; N_2 purged continuously during the test (except the air-equilibrated case).

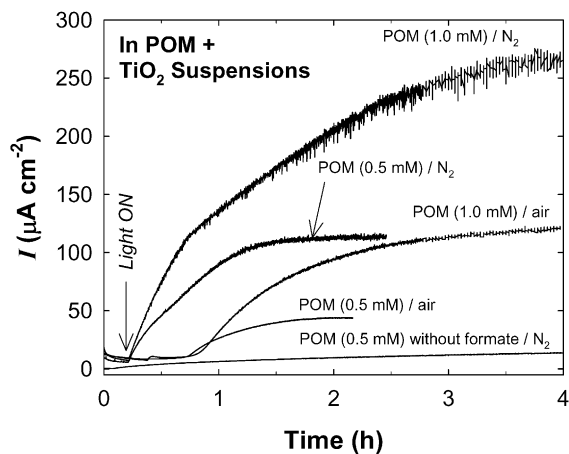


Figure 2. POM-mediated photocurrent generation in TiO_2 suspensions with or without dissolved O_2 . Experimental conditions were the following: $[\text{TiO}_2] = 0.5$ g/L; $[\text{formate}]_0 = 0.2$ M; continuously N_2 -purged or air-equilibrated; other conditions identical to those of Figure 1.

with its characteristic blue color, and the concentration of $[\text{POM}^-]$ was quantified by measuring the absorbance at $\lambda = 751$ nm. In the saturated current region where $dI/dt = 0$ (i.e., $d[\text{POM}^-]/dt = 0$), the fraction of the reduced POM, $[\text{POM}^-]_{\text{sat}}/[\text{POM}]_0$, is about 0.5 regardless of the initial POM concentration.

Figure 2 shows the profiles of photocurrent generation in the presence of both POM and TiO_2 (the case of Scheme 1b) where the currents are greatly enhanced compared with the POM only

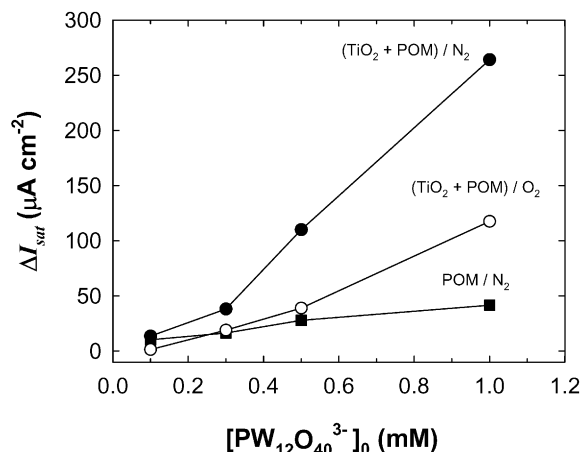


Figure 3. Dependence of the saturated photocurrents, ΔI_{sat} ($=I_{\text{light}} - I_{\text{dark}}$), on $[\text{POM}]_0$. Photocurrents in POM only under N_2 -saturation, POM + TiO_2 under N_2 -saturation, and POM + TiO_2 under air-equilibration are compared. Other experimental conditions were the same as those of Figure 1.

system. The dependence of the saturated currents on $[\text{POM}]_0$ is compared between the POM only and POM + TiO_2 systems in Figure 3. The apparent photonic efficiency (ϕ) in the POM (1 mM) + TiO_2 suspension is about 67% for $250 \mu\text{A cm}^{-2}$ current collected. The photocurrent generation in the TiO_2 suspension without POM is negligibly small ($<0.5 \mu\text{A cm}^{-2}$) (reaction T14). This indicates that photocurrent generated in the POM + TiO_2 suspension is not directly originated from CB electrons of TiO_2 . Although Bard and co-workers^{19,20} demonstrated that CB electrons in TiO_2 suspensions could be collected on an inert electrode, the current was very small ($<1 \mu\text{A cm}^{-2}$) in the absence of electron transfer mediators. Considering that most of the incident UV light should be absorbed or scattered by TiO_2 particles in this turbid suspension, the direct light absorption by POM in the TiO_2 suspension should be insignificant and the current via the Scheme 1a path should be minimal. This clearly indicates that POM should play the role of an efficient electron shuttle between the TiO_2 CB and the collector electrode as illustrated in Scheme 1b and that most photocurrents in Figure 2 are induced through this path (Scheme 1b). This successful role of POM as an electron shuttle should be ascribed to the fact that the electrons trapped in the POM molecule (as POM^-) are very long-lived whereas the CB electrons in TiO_2 particles are transient. Once the POM in aqueous solution was photoreduced in the presence of organic electron donors, the concentration of POM^- did not show any sign of decrease up to 2 h in the absence of dissolved oxygen.

The presence of dissolved oxygen in the TiO_2 suspension significantly delays and reduces the photocurrent generation, but does not completely inhibit it (Figures 2 and 3). After an induction period of about 40 min, the photocurrents start to rise and reach a plateau region in the TiO_2 suspension equilibrated with air. This fact implies either that O_2 scavenges most CB electrons on TiO_2 (reaction T9) or that the reduced POMs are rapidly reoxidized by O_2 (reaction T4) during the induction period. As POM is a more powerful electron acceptor than O_2 , the latter explanation (POM^- reoxidation via reaction T4) should be accepted. As long as O_2 molecules efficiently intercept electrons from the reduced POMs, few electrons are collected on the electrode. In other words, POMs mediate efficient electron transfers from the TiO_2 CB to O_2 molecules, which is the basis of the previous finding that the photocatalytic degradation of an organic compound on TiO_2 is highly enhanced in the presence of both POM and O_2 .¹⁶ As the dissolved or

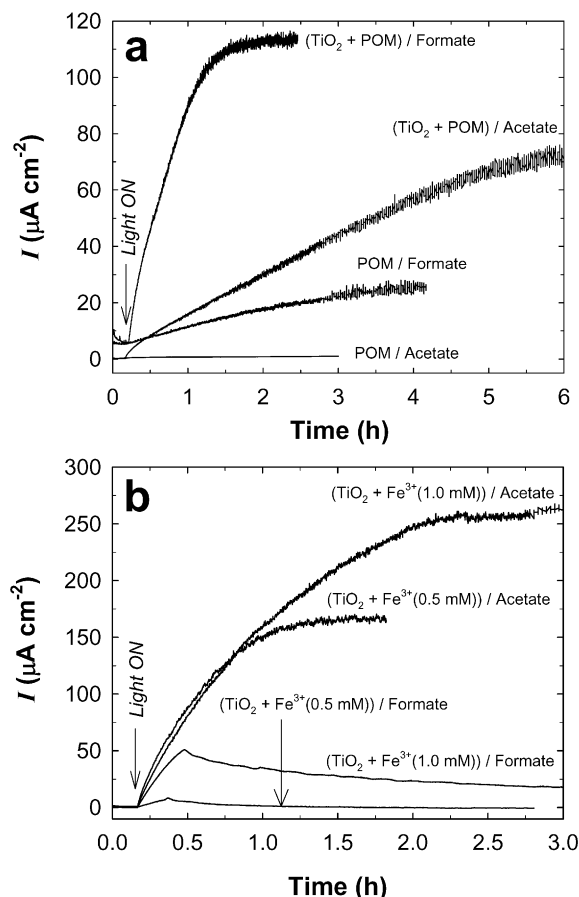
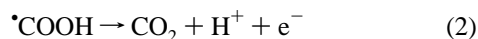


Figure 4. Effects of electron donors (formate vs acetate) on the photocurrent generation (a) in the POM only and the POM + TiO₂, and (b) in the Fe³⁺ + TiO₂ system. Experimental conditions were the following: [TiO₂] = 0.5 g/L; [PW₁₂O₄₀³⁻]₀ = 0.5 mM; [formate]₀ = [acetate]₀ = 0.2 M; continuously N₂-purged; other conditions identical to those of Figure 1.

adsorbed O₂ molecules in the suspension are consumed, the current rises slowly. The magnitude of *I*_{sat} in the air-equilibrated suspension is about half of that in the N₂-saturated suspension (Figure 3).

Effects of Electron Donors (Formate vs Acetate). Figure 4a compares the photocurrent generation in the POM solution and POM + TiO₂ suspension when formate or acetate is used as an electron donor. Formate induces a much faster current generation rate and a higher *I*_{sat} in both cases. This implies that the reactions of formate with excited POM (reaction T3) or TiO₂ VB holes (reaction T7) are faster than those of acetate. Since the POM solution with acetate does not show any sign of current generation, the rate of the reaction (POM* + acetate) should be negligibly slow. The higher *I*_{sat} value obtained in the POM + TiO₂ suspension with formate than that obtained with acetate could be ascribed to the well-known current doubling effect of formate (reactions 1 and 2).



However, when Fe³⁺ is used as an electron transfer mediator instead of PW₁₂O₄₀³⁻, acetate induces much higher photocurrents than formate (Figure 4b). In addition, the photocurrents generated in the presence of both Fe³⁺ and formate do not reach a saturation but start to decrease upon reaching a peak value.

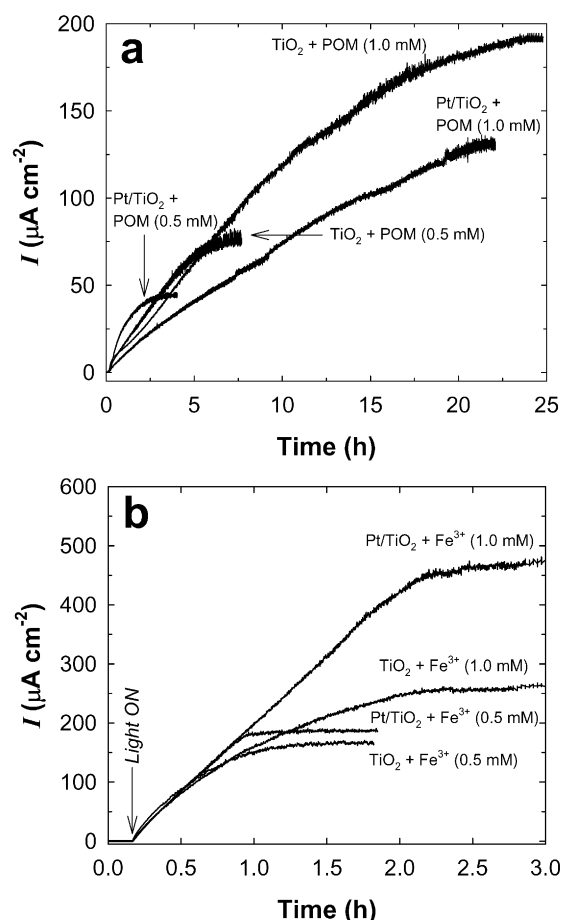
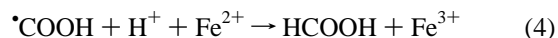
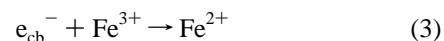


Figure 5. Comparison of photocurrent generation in UV-illuminated deoxygenated suspensions of (a) TiO₂ + PW₁₂O₄₀³⁻ and Pt/TiO₂ + PW₁₂O₄₀³⁻, and (b) TiO₂ + Fe³⁺ and Pt/TiO₂ + Fe³⁺ with acetate used as an electron donor. Experimental conditions were the following: [TiO₂] = [Pt/TiO₂] = 0.5 g/L; [acetate]₀ = 0.2 M; other conditions identical to those of Figure 1.

In agreement with this observation, the current-doubling effect in the photooxidation of 2-propanol on a TiO₂ electrode was reported to vanish in solutions containing Fe³⁺ probably because Fe³⁺ ions adsorbed on the TiO₂ surface enabled two-hole oxidation of 2-propanol through stabilizing the oxidation intermediates (or surface trapped holes).²¹ In this case, the Fe²⁺ ions that are produced from reacting with CB electrons (reaction 3) are thought to react with the formate radical (reaction 4). This makes a null cycle (short circuiting) and drastically reduces the electron shuttling efficiency of the Fe³⁺/Fe²⁺ couple.



In the presence of acetate, the corresponding reaction between acetate radical (·CH₂COOH) and Fe²⁺ should be insignificant.

Effects of Surface Platinization of TiO₂ on Electron Shuttling. The efficiencies of electron transfer from the TiO₂ CB to the collector electrode via the POM or Fe³⁺ mediator are compared in the suspensions of both naked TiO₂ and Pt/TiO₂. Acetate was used as an electron donor in this case to eliminate the current doubling effect of formate. Figure 5 shows that the current saturation is attained in a much shorter time with Fe³⁺ and that higher *I*_{sat} values are obtained also with Fe³⁺. A longer time needed for the current saturation in the POM + TiO₂ system indicates that the rate of electron scavenging from

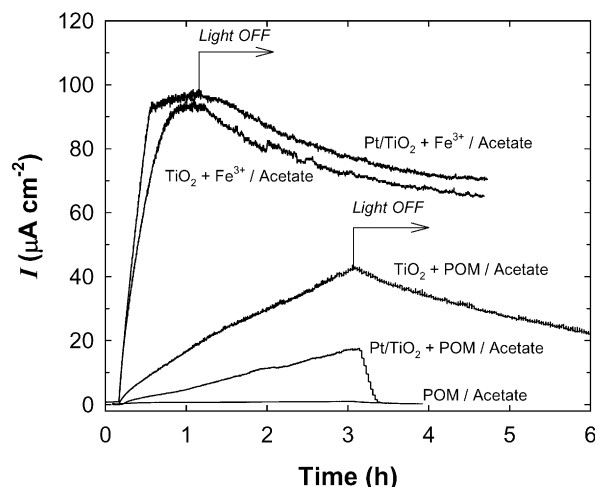


Figure 6. Comparison of photocurrent decay profiles upon turning off UV light. Experimental conditions were the following: [TiO₂] = [Pt/TiO₂] = 0.5 g/L; [Fe³⁺]₀ = [PW₁₂O₄₀³⁻]₀ = 0.3 mM; [acetate]₀ = 0.2 M; N₂-purged continuously during the test; other conditions identical to those of Figure 1.

the TiO₂ CB by POM is much slower than that of Fe³⁺. This might be ascribed to a higher driving force of electron abstraction from TiO₂ CB ($E_{CB} = -0.22$ V_{NHE} at pH 1.95) by the Fe³⁺/Fe²⁺ couple ($E^\circ = +0.77$ V_{NHE}) compared to that of the POM/POM⁻ couple ($E^\circ = +0.22$ V_{NHE}).

The electron shuttling efficiency of POM and Fe³⁺ in the TiO₂ suspension is significantly affected by whether the TiO₂ particles are platinized or not. POM is a better electron transfer mediator in naked TiO₂ than in Pt/TiO₂ suspension whereas the opposite trend is observed when Fe³⁺ is used as the electron shuttle. It is widely accepted that the platinization of the TiO₂ surface enhances the rate of interfacial electron transfer on TiO₂ by trapping CB electrons in the platinum phase and subsequently retarding the fast charge-pair recombination process.^{17,22,23} The electrons trapped in the Pt phase are thought to be more mobile (and loosely bound) than electrons trapped at TiO₂ surface sites.¹⁸ Therefore, the electron transfer to Fe³⁺ could be faster on Pt/TiO₂ than on a naked TiO₂ surface. However, this does not explain the lower electron transferring efficiency of POM on Pt/TiO₂. One possible explanation for this is a reduced electrostatic attraction between the positively charged TiO₂ surface (at pH 1.95) and the POM anions. The accumulation of electrons within the Pt phase creates negatively charged local surface sites and repels the POM anions (but attracts Fe³⁺ cations). However, the higher reactivity of the reduced POM with the Pt surface seems to be a more plausible explanation. It has been reported that a Pt catalyst accelerated both the reoxidation rate of the reduced POM and the hydrogen evolution rate in deaerated solution.^{24–26} This indicates that the presence of Pt surface facilitates the reduction of H⁺ (reaction 5), which should reduce the POM-mediated current as shown in Figure 5a.

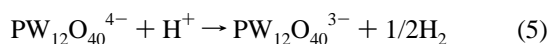


Figure 6 compares the current decay profiles in the TiO₂ and Pt/TiO₂ suspension after the light illumination is turned off. With Fe³⁺ as an electron transfer mediator, current decrease profiles are little different between the TiO₂ and Pt/TiO₂ suspension. However, with using POM instead of Fe³⁺, current in the Pt/TiO₂ suspension is rapidly extinguished as soon as light is off, which is not observed in the naked TiO₂ suspension. This

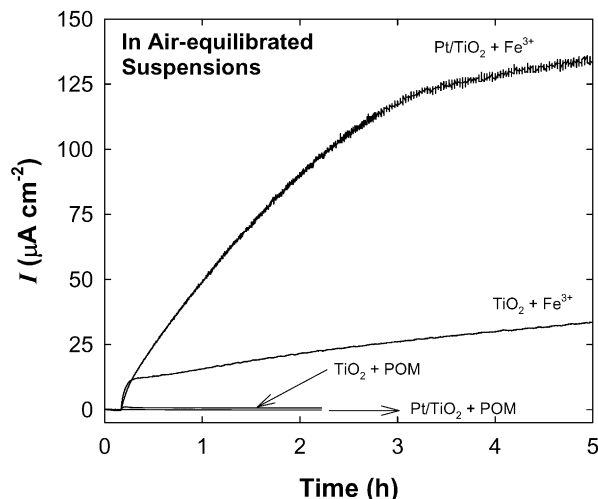


Figure 7. Comparison of photocurrent generation in air-equilibrated TiO₂ and Pt/TiO₂ suspensions with POM or Fe³⁺. Experimental conditions were the following: [TiO₂] = [Pt/TiO₂] = 0.5 g/L; [Fe³⁺]₀ = [PW₁₂O₄₀³⁻]₀ = 0.5 mM; [acetate]₀ = 0.2 M; air-equilibrated; other conditions identical to those of Figure 1.

confirms that the Pt surface catalyzes the reoxidation of the photoreduced POM through reaction 5. While the POM addition alone or the surface platinization alone increases the efficiency of CB electron transfer in TiO₂ photocatalysis, the combination of both in fact decreases the overall electron transfer efficiency.

Effect of Dioxygen. Figure 7 compares the current generation profiles in the “air-equilibrated” TiO₂ (or Pt/TiO₂) suspensions with POM or Fe³⁺ when acetate is used as an electron donor. No current is generated in the POM + TiO₂ system whether the TiO₂ surface is platinized or not. This is compared with the case of formate used as an electron donor (Figures 2 and 3), in which the photocurrent is generated even in the “air-equilibrated” POM + TiO₂ suspension after an induction period. The role of formate through the current doubling seems to be critical in generating the photocurrent in the presence of O₂. On the other hand, Fe³⁺ ions induce significant photocurrents even in the presence of dissolved oxygen. This reflects that the reoxidation of Fe²⁺ by O₂ is very slow at low pH. The second-order rate constant of Fe²⁺ + O₂ (reaction T11) at pH < 3 is about $2 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$,²⁷ while that of POM⁻ + O₂ (reaction T4) is $75 \text{ M}^{-1} \text{ s}^{-1}$.¹¹ With these rate constants and [O₂] = $2 \times 10^{-4} \text{ M}$ (air-equilibrated concentration), the half-lives of Fe²⁺ and POM⁻ are 2006 days and 46 s, respectively. Therefore, the reoxidation reaction of Fe²⁺ by O₂ is negligible in the present experimental conditions. From another point of view, this indicates that Fe³⁺ ions do not transfer the CB electrons to O₂ at all whereas POMs mediate the electron transfer to O₂ very effectively, which is often the rate limiting step in the overall kinetics of photocatalytic reactions.

The fact that the magnitude of Fe³⁺-mediated current is reduced by the presence of O₂ indicates (compare Figures 5b and 7) that both Fe³⁺ and O₂ are competing for CB electrons (reactions T10 vs T9). The platinization of TiO₂ significantly enhances the Fe³⁺-mediated photocurrent generation in the air-equilibrated suspension as does in the N₂-saturated suspension (Figure 5b). This implies that the relative rate ratios of CB electron transfer to Fe³⁺ versus O₂ (r_{T10}/r_{T9}) are different on the naked and platinized TiO₂ surface. The rate ratio should be higher on Pt/TiO₂ than on naked TiO₂. In other words, the CB electron transfer to Fe³⁺ is relatively more favored on Pt/TiO₂ although the absolute rate of electron transfer to O₂ is also enhanced on Pt/TiO₂.²⁸ In accordance with this, Kim and Choi

recently reported that the relative rate ratios of CB electron transfer to trichloroacetate versus O₂ strongly depended on whether TiO₂ surface was platinized or not.²²

Conclusions

The electron transfer mediating ability of POMs in aqueous solution or TiO₂ suspension under UV illumination is directly demonstrated by monitoring the photocurrent generation. POMs successfully mediate electron transfers from the TiO₂ CB to a collector electrode, and their performance as an electron shuttle is compared with that of Fe³⁺ ions. Although POMs are less efficient than Fe³⁺ in mediating the photocurrent generation in general, they exhibit a unique behavior different from Fe³⁺. The relative effects of electron donors and platinization of TiO₂ on the POM-mediated current generation (reaction T12) are opposite to those on the Fe³⁺-mediated current (reaction T13). In the presence of dissolved O₂ and acetate as an electron donor, the POM-mediated current is completely extinguished due to the rapid reoxidation of the reduced POMs by O₂ whereas significant photocurrents are still generated through the Fe³⁺-mediated pathway. This indicates that POMs are very efficient in transferring CB electrons on TiO₂ particles to O₂ molecules. Accordingly, in air-equilibrated TiO₂ suspensions in which most photocatalytic reactions have been investigated, the addition of POMs that mediate the CB electron transfer to O₂ enhances the overall rate of photocatalytic oxidation reaction.¹⁶ Understanding the electron transfer mediating behaviors of POMs should be essential when they are used in TiO₂ photocatalysis for better photoefficiencies.

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References and Notes

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