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Study of special cases where the enhanced photocatalytic activities of Pt/TiO_2 vanish under low light intensity

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Abstract

Surface platinized TiO_2 (Pt/TiO_2) has been widely used and investigated but their properties are yet to be understood fully. Although it is known that the Pt effects depend on many experimental parameters and the kind of substrates, this study newly finds that the Pt effects could be also influenced by the light intensity. As for the photocatalytic degradation of trichloroethylene (TCE), the Pt effect was positive at high light intensity but was negative at low light intensity. A similar behavior was also observed in the photocurrent collection in the Pt/TiO_2 suspension with polyoxometalate (POM: $PW_{12}O_{40}{}^{3-}$) used as an electron shuttle. The photocurrent collection in the Pt/TiO_2 suspension was less efficient than in TiO_2 suspension when the light intensity was low. Such abnormal light intensity-dependent behaviors were not observed in the photocatalytic degradation of dichloroacetate on Pt/TiO_2 and the Fe^{3+}-mediated photocurrent collection in the Pt/TiO_2 suspension. It is proposed that the photochemical interactions between the Pt surface and reactive intermediates (TCE radical anions and reduced POM anions) induce a null reaction favorably at low light intensity condition.

Keywords: Photocatalyst; TiO_2; Surface platinization; Photocurrent; Polyoxometalate; Light intensity effect

1. Introduction

TiO_2 photocatalysis has been intensively investigated for environmental remediation and energy conversion [1–9]. Because the efficiency of TiO_2 photocatalytic reactions is largely determined by interfacial charge transfers, various surface modification methods have been developed to facilitate the charge transfer. Among them the most popular is the surface platinization of TiO_2 [10–15]. The roles of Pt nanoparticles deposited on TiO_2 surface are multiple: they retard fast electron–hole pair recombination by serving as an electron sink (i.e. Schottky barrier electron trapping) [3] and subsequently facilitate the interfacial electron transfer [16], widen the spectral response to longer wavelengths by introducing Pt-derived electronic states [17], and alter the photocatalytic reaction mechanism by providing catalytic sites [18,19].

As for the effects of surface platinization on the photocatalytic reactivity, both positive and negative effects have been reported [20,21]. Sometimes, the reported Pt effects are contradictory even for the same substrate [22–24]. Our recent study revealed that the Pt effects on photocatalytic activities are highly substrate-specific and sensitively depend on the properties of Pt deposits such as Pt oxidation state [25]. The photocatalytic degradation of trichloroethylene (TCE) was significantly inhibited when oxidized Pt species (Pt_{ox}) instead of Pt^0 was deposited on TiO_2 whereas such a drastic activity reduction with Pt_{ox}/TiO_2 was not observed for other substrates. It was suggested that the Pt effects in photocatalysis depend on the Pt-substrate interaction as well as the properties of Pt deposits (e.g. loaded amount, oxidation state, size, etc.).

In this study, we demonstrated that the Pt effects could depend on the light intensity as well. Surface platinization of TiO_2 enhanced the photocatalytic activity of TCE degradation at high light intensity but retarded it on the contrary at lower light intensity. Similar light intensity-dependent behavior was also observed in the photocurrent collection in the suspension of Pt/TiO_2 + polyoxometalate (as an electron shuttle). Experimental evidences are presented and discussed for the special cases where the Pt effects in Pt/TiO_2 photocatalysis vanish. The effects of

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surface platinization of TiO_2 in photocatalysis are yet to be understood fully despite extensive studies on Pt/TiO_2.

2. Experimental

2.1. Materials and reagents

TiO_2 powder (Degussa P25), a mixture of anatase and rutile (8:2), was used as a base photocatalyst. Pure anatase powder (Hombikat UV-100) and pure rutile powder (Aldrich) were also used for comparison. Trichloroethlyene (TCE, $CCl_2{=}CHCl$, Junsei) and sodium dichloroacetate (DCA, $CHCl_2CO_2Na$, Aldrich) was used as substrates for photocatalytic degradation. $PW_{12}O_{40}{}^{3-}$ (a polyoxometalate (POM), Sigma) and Fe^{3+} ($FeCl_3{\cdot}6H_2O$, Kanto) were used as an electron acceptor, and acetate (CH_3CO_2Na, Merck) as an electron donor. Water used was ultra-pure (18 MΩ cm) and prepared by a Barnstead purification system. For Pt/TiO_2 preparation, an aqueous TiO_2 suspension (0.5 g/L) containing 1 M methanol and 0.1 mM hexachloroplatinic acid ($H_2PtCl_6{\cdot}6H_2O$, Aldrich) was irradiated with a 300 W mercury UV 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. Pt particles deposited on TiO_2 under this condition was found to exist as a form of Pt^0, which was confirmed by XPS analysis, and their size analyzed by transmission electron microscopy was in the range 2–10 nm [25]. A typical Pt loading on TiO_2 was estimated to be ca. 3 wt.% by comparing the chloroplatinate concentration in solution before and after the photodeposition.

2.2. Photocatalytic oxidation on Pt/TiO_2

The photocatalytic oxidation of TCE and DCA was performed using a 60 mL Pyrex reactor with a quartz window. Saturated TCE stock solution (8.4 mM) and DCA stock solution (10 mM) were prepared in distilled water. The TiO_2 (or Pt/TiO_2) suspension concentration was 0.5 g/L and the concentrations of TCE and DCA in the suspension were adjusted to 0.5 and 1.0 mM, respectively. The initial suspension pH was adjusted to 4.0. The photocatalytic reactor was filled with minimized headspace, sealed with a rubber septum, and stirred magnetically. The light source was a 300 W Xe-arc lamp (Oriel). Light passed through a 10 cm IR water filter and a UV cutoff filter ($\lambda > 300$ nm), and then was focused onto the quartz window of the reactor. The light intensity was varied by interposing a neutral density filter (transmittance (T) of 32, 10 and 1%) between the cutoff filter and the reactor. The focused light intensity was ca. 200 mW/cm^2 without any neutral density filter (T100%). The light intensity was measured using a power meter (Newport 1830-C) equipped with a silicon diode detector. Sample aliquots were withdrawn from the illuminated reactor with a 1 mL syringe, filtered through a 0.45 μm PTFE filter (Millipore), and injected into a 2 mL glass vial. Quantitative analysis of chloride ions generated from the degradation of TCE and DCA was performed by using an ion chromatography (IC, Dionex DX-120). The IC system was equipped with a Dionex IonPac AS-14 for anions and a conductivity detector.

2.3. Photocurrent collection with Pt/TiO_2

In the photocatalytic current collection experiments, TiO_2 (or Pt/TiO_2) was suspended at 0.33 g/L in a glass reactor. $PW_{12}O_{40}{}^{3-}$ (or Fe^{3+}) (0.1 mM) and sodium acetate (0.1 M) were added to the suspension as an electron shuttle and an electron donor, respectively. The UV-induced current collection in the Pt/TiO_2 suspension is illustrated in Scheme 1 [16]. The suspension pH was adjusted to ca. 1.2 with $HClO_4$. A platinum plate (1 cm × 1 cm, 0.125 mm thick, both sides exposed to the solution, Aldrich), a saturated calomel electrode (SCE), and a graphite rod were immersed in the reactor as a working (electron collector), reference, and counter electrode, respectively. N_2 gas was vigorously (ca. 50 cm^3/min) purged through the suspension using a gas dispenser for 30 min prior to and during UV irradiation. The light source was the 300 W Xe arc lamp. Photocurrents generated in the suspension were measured with applying a potential (+0.6 V versus SCE) to the Pt working electrode using a potentiostat (EG&G 263A2).

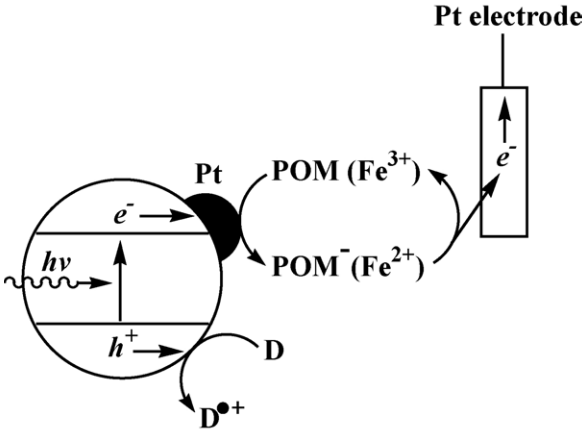
3. Results and discussion

3.1. Effect of light intensity on the photocatalytic degradation on Pt/TiO_2

Fig. 1 compares the chloride production from the photocatalytic degradation of DCA and TCE in TiO_2 (Degussa P25) or Pt/TiO_2 suspension under different light intensities. For both substrates, their photocatalytic degradation on TiO_2 leads to complete mineralization with producing chlorides and carbon dioxide as final products [18,26]

$$CHCl_2CO_2{}^- + O_2 \rightarrow 2CO_2 + H^+ + 2Cl^- \quad (1)$$

$$CHCl{=}CCl_2 + H_2O + 1.5O_2 \rightarrow 2CO_2 + 3H^+ + 3Cl^- \quad (2)$$



Scheme 1. Electron shuttle (POM or Fe^{3+})-mediated photocurrent collection on a Pt electrode immersed in UV-illuminated Pt/TiO_2 suspension.

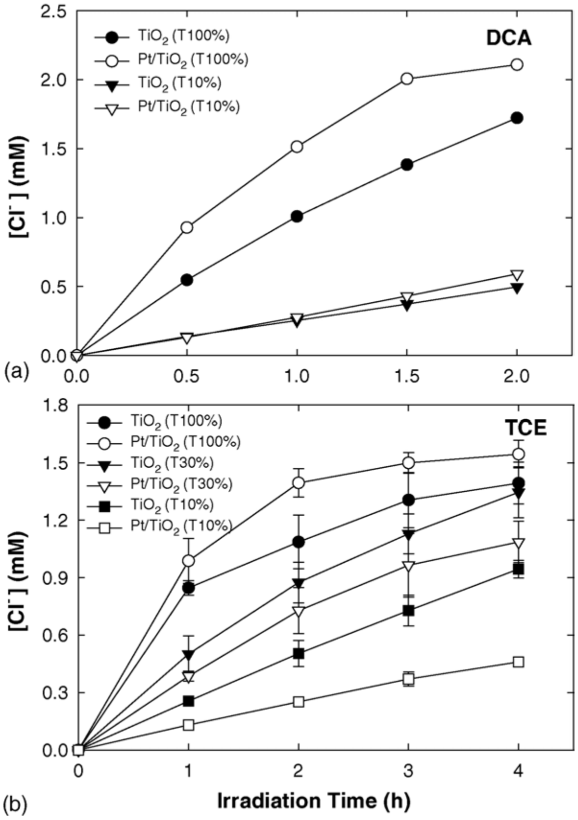


Fig. 1. Photocatalytic degradation of (a) DCA and (b) TCE in naked TiO$_2$ and Pt/TiO$_2$ suspensions under different UV intensities. Degussa P25 was used as TiO$_2$. [TiO$_2$] = [Pt/TiO$_2$] = 0.5 g/L; [DCA]$_0$ = 1.0 mM; [TCE] = 0.5 mM; pH$_i$ = 4.0;. T denotes UV transmittance of neutral density filter. At T100%, T30%, and T10%, UV light ($\lambda > 300$ nm) intensity was 200, 60, and 20 mW/cm^2, respectively.

As for DCA degradation, the initial dechlorination rate under T100% intensity was faster with Pt/TiO$_2$ than TiO$_2$ whereas TiO$_2$ and Pt/TiO$_2$ under T10% intensity showed little difference in the dechlorination rate. That is, the Pt enhancement effect was not observed under the lower light intensity. Such a ‘‘light intensity-dependent Pt effect’’ is more outstanding in the case of TCE degradation (Fig. 1b) where the order of reactivity between TiO$_2$ and Pt/TiO$_2$ was reversed at T30% and T10% conditions. The Pt effect on TCE degradation was slightly positive at T100% but negative at T30% and T10%. Comparison of Figs. 1 and 2 shows that the Pt effect is dependent on the kind of TiO$_2$ as well. In the TCE–rutile system, the Pt effect is nearly absent at T100% and even negative at T10% while the Pt effect is consistently positive regardless of the light intensity in the TCE–anatase system. Previous studies on the photocatalytic degradation of TCE on Pt/TiO$_2$ have reported inconsistent results because the activity of Pt/TiO$_2$ photocatalyst widely varies depending on the properties of Pt deposits and the nature of Pt–substrate interactions [22–25]. For example, TiO$_2$ particles loaded with platinum oxides was almost completely inactive for TCE degradation but TiO$_2$ with Pt^0 species was as active as naked TiO$_2$ [25]. This study reveals additional complexity in the photocatalytic activity of Pt/TiO$_2$. The Pt effects can be dependent on the light intensity and the kind of TiO$_2$ substrate, which is particularly prominent for the case of TCE degradation. Specific interaction between TCE degradation intermediates and TiO$_2$ surface sites whose characteristics might vary with the kind of commercial TiO$_2$ sample seems to influence its photocatalytic reaction significantly. Such abnormal Pt effects do not seem to be associated with DCA degradation.

3.2. Effect of light intensity on the photocurrent collection in Pt/TiO$_2$ suspensions

Photocurrents can be collected on an inert Pt electrode immersed in the UV-illuminated TiO$_2$ or Pt/TiO$_2$ suspensions when suitable electron shuttles such as Fe^{3+} or POM (e.g. PW$_{12}$O$_{40}$$^{3-}$) are present [16]. When the surface of TiO$_2$ is platinized, the current collection efficiency is expected to increase because of the conduction band (CB) electron trapping in the Pt deposits. As more CB electrons are trapped in the Pt phase, more should be transferred to the collector electrode via the redox cycle of electron shuttles. Fig. 3 compares the time profiles of photocurrent generation in TiO$_2$ (P25) and Pt/TiO$_2$ suspensions in the presence of Fe^{3+} or PW$_{12}$O$_{40}$$^{3-}$ as an electron shuttle under different light intensities. Fe^{3+}-mediated photocurrent generation in the Pt/TiO$_2$ suspension was consistently more efficient than that in the TiO$_2$ suspension under all irradiation conditions. Ferric ions scavenge CB electrons very efficiently from the illuminated Pt/TiO$_2$ surface. Note that the photocurrent generation with Pt/TiO$_2$ at T10% was higher than that obtained with TiO$_2$ at T100%. The platinization-enhanced current increase is far more outstanding at T10% than at T100% (Fig. 3a), which indicates that the enhancement effect is higher when the photon flux is limited. Under higher light intensity, the number of excited charge pairs approaches a saturation level, and so does the collection current. Therefore, the Pt-enhancement effect is relatively small at T100%. On the other hand, for the POM-mediated photocurrent generation (Fig. 3b), the current with Pt/TiO$_2$ was slightly lower than that obtained with TiO$_2$ under low light intensities (T10% and T1%). That is, the effect of platinization on the POM-mediated current collection switches from positive to negative when the light intensity was lowered. Fig. 4 shows that similar behaviors of the photocurrent collection were also observed in the pure anatase or pure rutile suspension with Fe^{3+} or POM.

The photocurrent profiles in Figs. 3 and 4 can be quantitatively expressed as follows:

$$I = \alpha[\mathrm{S}^-] \tag{3}$$

$$[\mathrm{S}^-] = [\mathrm{S}]_0(1 - \mathrm{e}^{-kt}) \tag{4}$$

$$I = \alpha[\mathrm{S}]_0(1 - \mathrm{e}^{-kt}) \tag{5}$$

where I is the photocurrent density (μA cm^{-2}), α a constant related to electrochemical properties, S and S$^-$ are the electron shuttle (Fe^{3+}/Fe^{2+}; PW$_{12}$O$_{40}$$^{3-}$/PW$_{12}O_{40}$$^{4-}$), and k is the reduction rate constant (min^{-1}) of S on illuminated TiO$_2$. k values can

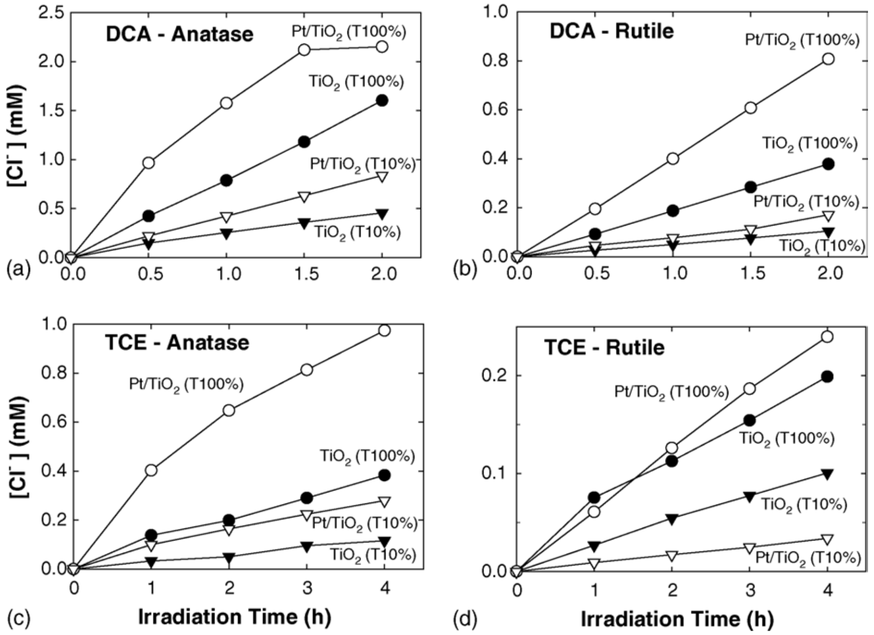


Fig. 2. Photocatalytic degradation of (a) DCA with anatase and Pt/anatase, (b) DCA with rutile and Pt/rutile, (c) TCE with anatase and Pt/anatase, and (d) TCE with rutile and Pt/rutile at T100% and T10% condition. Hombikat UV-100 and Aldrich rutile were used as anatase and rutile, respectively. Other conditions were identical to those of Fig. 1.

be obtained by fitting the time profile of photocurrent (as in Fig. 3) to Eq. (5). Fig. 5 shows the variation of k values (obtained from the fitting) as a function of the light intensity. Fe^{3+}-mediated and POM-mediated photocurrent generation are clearly different in their light intensity dependence. In the Fe^{3+}-mediated case, $\log(k)$ is proportional to $\log(I)$ in the entire intensity region whereas the light intensity dependence in the POM-mediated case is very different between the low and high intensity region. It is well known that the quantum yields of photocatalytic reactions depend on the light intensity: the rate of charge–pair recombination is slower and the quantum yield is higher when fewer electron–hole pairs are present in the semiconductor particle (i.e. in the low light intensity condition) [1–3]. In general, the photocatalytic rate constant (k_{ph}) is proportional to I^n. It has been frequently reported that n values range between 0.5 and 1.0 in a variety of photocatalytic reactions: $n = 1.0$ at low light intensity limit and $n = 0.5$ at high light intensity limit [27,28]. The variation in n values is usually related with the light intensity-dependent kinetics of charge recombination. However, the marked transition in the light intensity dependence that is observed in this POM-mediated photocurrent generation system should not be due to the charge recombination kinetics because the identical photocatalyst does not exhibit such behavior in the Fe^{3+}-mediated photocurrent generation. Some special interaction of POM with the photocatalyst surface might be involved, which is discussed in the following section.

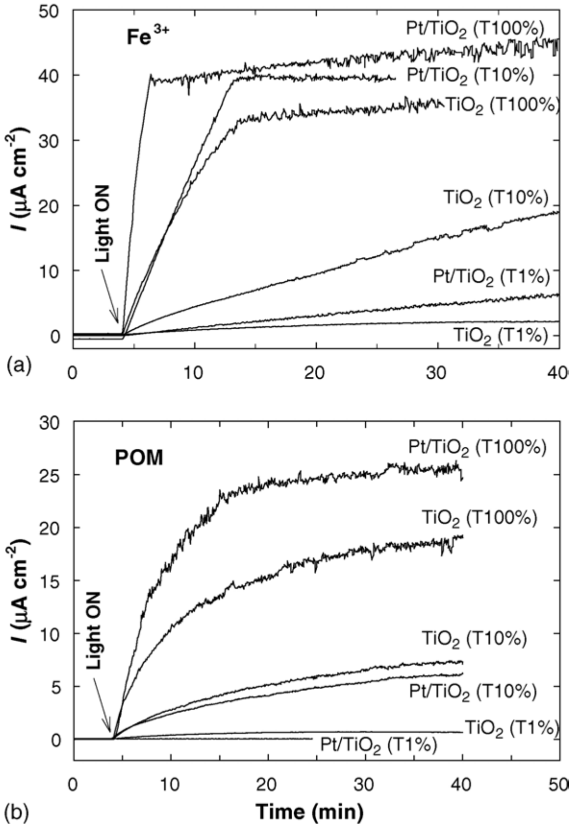


Fig. 3. Comparison of photocurrent generation in UV-illuminated deoxygenated suspensions of (a) $TiO_2 + Fe^{3+}$ and $Pt/TiO_2 + Fe^{3+}$, and (b) $TiO_2 + PW_{12}O_{40}^{3-}$ and $Pt/TiO_2 + PW_{12}O_{40}^{3-}$ with acetate (electron donor). $[TiO_2] = [Pt/TiO_2] = 0.33$ g/L; $[acetate]_0 = 0.1$ M; $[Fe^{3+}] = [PW_{12}O_{40}^{3-}] = 0.1$ mM; pH = 1.2; continuously N_2-purged with 50 cm^3/min; the Pt collector electrode held at +0.6 V (vs. SCE). Degussa P25 was used as TiO_2.

3.3. Understanding the abnormal light intensity-dependent Pt effects

The abnormal light intensity-dependent behaviors observed in the TCE degradation on Pt/TiO_2 and the POM-mediated

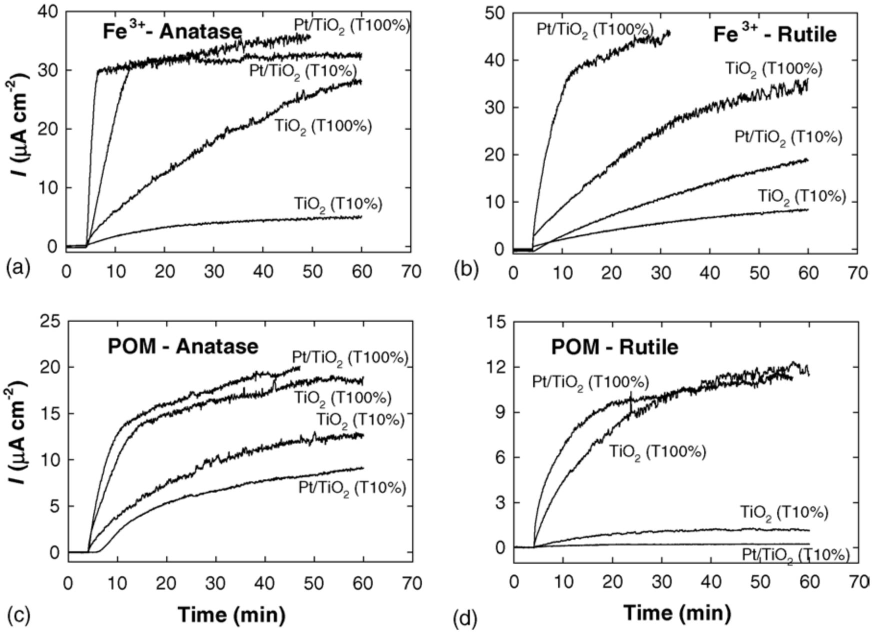


Fig. 4. Comparison of photocurrent generation in UV-illuminated suspensions of (a) anatase and Pt/anatase with Fe^{3+} (b) rutile and Pt/rutile with Fe^{3+} (c) anatase and Pt/anatase with POM and (d) rutile and Pt/rutile with POM. Hombikat UV-100 and Aldrich rutile were used as anatase and rutile, respectively. Other conditions were identical to those of Fig. 3.

photocurrent collection in Pt/TiO_2 suspension cannot be explained by the general role of Pt deposits in charge separation (Scheme 2a) because such behaviors are peculiar to special cases and substrate-specific. In both cases, the Pt effects on the photocatalytic activity are positive at higher light intensities but reversed to negative at lower light intensities.

Since the light intensity-dependent Pt effects were substrate-specific, the most plausible explanation might be that the photochemical interactions between the Pt surface and reactive intermediates are affected by the light intensity. We recently proposed that the photocatalytic degradation of TCE on Pt/TiO_2 could be significantly inhibited when the TCE-mediated recombination path is operative as illustrated in Scheme 2b [25]. TCE radical anions ($TCE^{\bullet-}$) could be generated after accepting CB electrons and stabilized on the Pt surface. A reductive degradation path via $TCE^{\bullet-}$ formation might follow. The existence of this path was supported from the fact that the TCE degradation in the deaerated suspension was highly enhanced in the presence of Pt^0 deposits on TiO_2 [25]. When $TCE^{\bullet-}$ on the Pt surface successively reacts with a VB hole, a null reaction (TCE-mediated recombination) results and the overall efficiency of TCE degradation is reduced. Once $TCE^{\bullet-}$ is desorbed from the Pt surface into the liquid bulk, it immediately reacts with O_2 to be degraded and has little chance to re-adsorb on the naked portion of TiO_2 surface. Therefore, the oxidation of $TCE^{\bullet-}$ (i.e. recombination) should take place preferably on the Pt surface. It seems that this null reaction path occurring on Pt/TiO_2 is favored under low light intensity. The reason might be as follows. At photo-stationary state, Pt nanoparticles on TiO_2 can store electrons in them and hence be negatively charged. The electron storing capacity of metal nanoparticles in contact with photoexcited TiO_2 nanoparticles

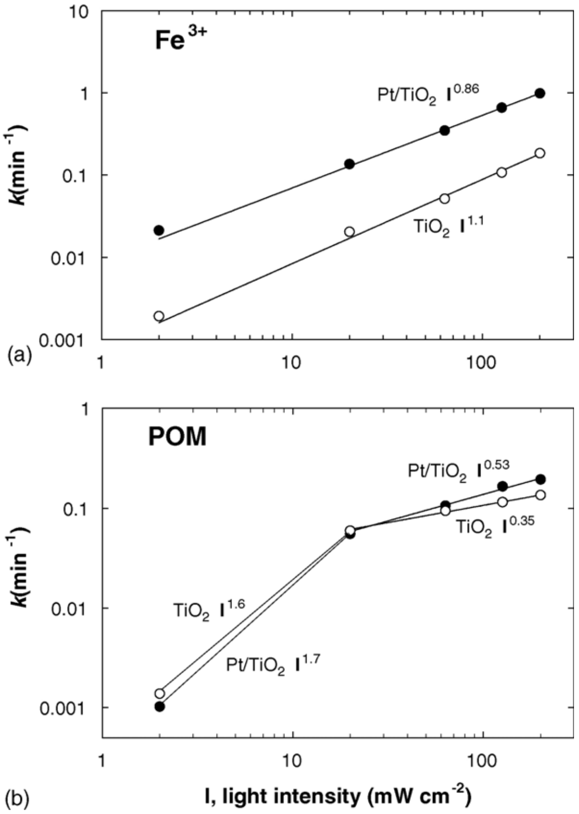
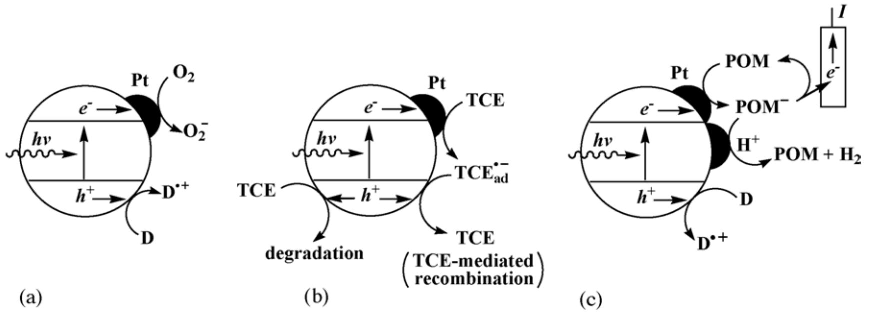


Fig. 5. The first-order rate constants (k) of the photoreduction of S (Fe^{3+} or POM) on TiO_2 as a function of the light intensity in (a) Fe^{3+}-mediated and (b) POM-mediated photocurrent generation systems. k values were obtained by fitting the time profile of photocurrent (as in Fig. 3) to Eq. (5). Experimental conditions were identical to those of Fig. 3.



Scheme 2. Illustrative comparison of different cases of photoinduced charge transfers taking place on a Pt/TiO$_2$ particle. (a) A typical case where the enhanced charge separation due to electron trapping in the Pt deposit increases the rate of photocatalytic oxidation of substrates (D). (b) A case where the TCE-mediated recombination on Pt/TiO$_2$ reduces the overall efficiency of photocatalytic TCE degradation. (c) A case where the catalytic reoxidation of POM$^-$ on Pt/TiO$_2$ decreases the efficiency of photocurrent collection on a Pt electrode.

has been demonstrated [29]. It is expected that more electrons should be stored in the Pt phase with increasing the light intensity. As a result, the Pt surface is more negatively charged under high intensity illumination and less stabilizes TCE$^{•-}$ anions because of the enhanced electrostatic repulsion. This implies that the TCE-mediated recombination path on Pt/TiO$_2$ is insignificant when the light intensity is high. However, its contribution to the overall mechanism cannot be neglected when the light intensity is low. In such case, Pt/TiO$_2$ could have a lower activity for TCE degradation than TiO$_2$.

The light intensity-dependent behaviors in the POM-mediated photocurrent generation can be explained in a similar way. POM$^-$ anion is generated upon accepting a CB electron, which is subsequently reoxidized at the surface of Pt electrode. When Pt deposits are present on the surface of TiO$_2$, the surface Pt sites provide an additional reoxidation path (reaction (6)) [16]

$$\mathrm{PW_{12}O_{40}}^{4-}(\mathrm{Pt}) + \mathrm{H}^+ \rightarrow \mathrm{PW_{12}O_{40}}^{3-}(\mathrm{Pt}) + (1/2)\mathrm{H_2} \qquad (6)$$

The situation is illustrated in Scheme 2c. Owing to reaction (6), the current decay profiles in the Pt/TiO$_2$ suspension upon turning off the UV illumination are very different between the Fe^{3+}-mediated and POM-mediated systems (see Fig. 6). With Fe^{3+} as an electron shuttle, the current decay profiles are little different between the TiO$_2$ and Pt/TiO$_2$ suspensions. However, when using POM instead of Fe^{3+}, the current in the Pt/TiO$_2$ suspension is more rapidly extinguished because of the action of reaction (6). The reoxidation of Fe^{2+} taking place on Pt/TiO$_2$ (similar to reaction (6)) seems to be insignificant probably because Fe^{2+} is much harder to oxidize than POM$^-$ [E^0(Fe^{3+}/Fe^{2+}) = 0.77 V$_{\mathrm{NHE}}$ versus E^0(POM/POM$^-$) = 0.22 V$_{\mathrm{NHE}}$]. The light intensity dependence in the POM-mediated current generation seems to be related with the reoxidation step occurring on the Pt surface. The accumulation of electrons in the Pt phase induces negative surface charge that should increase with the light intensity. According to the similar logic applied to the Pt/TiO$_2$–TCE system, the reoxidation of POM$^-$ on Pt/TiO$_2$ surface (reaction (6)) is insignificant under high light intensities because of the enhanced electrostatic repulsion but could hinder the current collection process when the light intensity is low. When the role of reaction (6) is significant under low intensity illumination, the photocurrent collection in the Pt/TiO$_2$ suspension could be less efficient than in TiO$_2$ suspension.

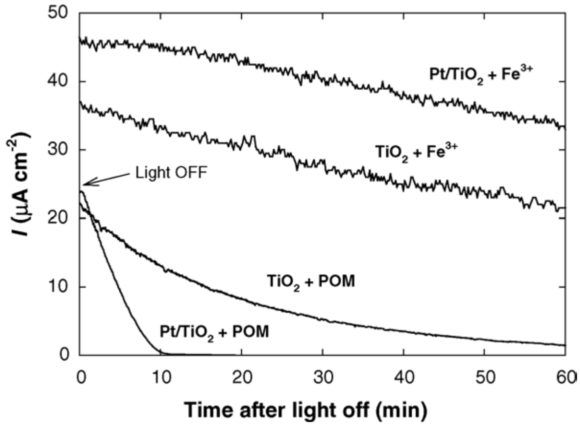


Fig. 6. Comparison of current decay profiles upon turning off UV light (after the photocurrent profiles reached the plateau region at T100% condition) in TiO$_2$ + Fe^{3+}, Pt/TiO$_2$ + Fe^{3+}, TiO$_2$ + POM and Pt/TiO$_2$ + POM suspensions. Experimental conditions were identical to those of Fig. 3.

4. Conclusions

This study reports peculiar cases where the Pt effects in TiO$_2$ photocatalysis vanish at low light intensities. The Pt effects observed in many TiO$_2$ photocatalytic reactions are substrate-specific, influenced by properties of Pt deposits (Pt loading, particle size, Pt oxidation state, etc.), and hard to generalize. Although previous studies addressed various aspects of Pt/TiO$_2$ photocatalysis, the fact that the Pt enhancement effect that is observed at high light intensity can vanish (or even reverse to an adverse effect) under low intensity illumination has not been recognized before. Photocatalytic degradation of TCE on Pt/TiO$_2$ and the POM-mediated photocurrent generation in Pt/TiO$_2$ suspension show such abnormal light-intensity dependent behavior. The photochemical interactions between the Pt surface and reactive intermediates (TCE radical anions and reduced POM anions) seem to be affected by the light intensity. It is proposed that both intermediate radical anions react on the

Pt surface to induce a null reaction, which is favored at low light intensity condition.

Acknowledgements

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