Activation of peroxymonosulfate on visible light irradiated TiO$_2$ via a charge transfer complex path

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HIGHLIGHTS

- PMS serves as a complexing ligand and a radical precursor in the activation process.
- Visible light irradiation activates PMS on TiO$_2$ via ligand-to-metal charge transfer.
- The TiO$_2$/PMS/visible light system shows catalytic performance in organic oxidation.

ABSTRACT

Photo-induced activation of peroxymonosulfate (PMS) has been enabled by either the direct photolysis of the peroxide bond or the semiconductor bandgap-excited photocatalysis. Whereas the existing approaches utilize UV light, this study first studied the utilization of visible light for the PMS activation in which the dual roles of PMS as a complexing ligand on TiO$_2$ and a precursor of sulfate radical (SO$_4^{2-}$) are enabled via ligand-to-metal charge transfer (LMCT) mechanism. In this LMCT-mediated photocatalysis, PMS coordinated to TiO$_2$ as a surface complex is photoexcited by visible light to inject electrons to the CB of TiO$_2$, which subsequently activate PMS to yield SO$_4^{2-}$.

Despite the lack of visible light activity of both TiO$_2$ and PMS, the addition of PMS induced a significant degradation of 4-chlorophenol and dichloroacetate on TiO$_2$ under visible light irradiation. Together with several spectroscopic analyses, the result revealed the formation of an interfacial charge transfer (CT) complex of PMS on TiO$_2$ and the LMCT-mediated PMS conversion into SO$_4^{2-}$. Multi-activity assessment showed that the oxidizing capacity of TiO$_2$/PMS varied depending on the substrate type; benzoic acid and acetaminophen were rapidly decomposed whereas nitrophenol oxidation was insignificant. The role of SO$_4^{2-}$ as the main oxidant was identified based on (1) quenching effect of methanol as a radical quencher, (2) coumarin...
hydroxylation as an indication of SO$_4^{2−}$ formation, and (3) EPR spin-trapping technique. The comparison of TiO$_2$/PMS versus Co$_3$O$_4$/PMS suggested that the repeated acetaminophen decay was achievable with TiO$_2$/PMS without the loss of activating capacity whereas a gradual reduction in degradation efficiency was observed with Co$_3$O$_4$/PMS.

1. Introduction

Persulfate (collectively representing peroxymonosulfate (PMS; HSO$_5^−$) and peroxydisulfate (PDS; S$_2$O$_8^{2−}$)) activation has been demonstrated to rapidly degrade a wide range of organic pollutants possessing different chemical structures through the production of sulfate radical (SO$_4^{2−}$) as a highly reactive intermediate (E$^0$(SO$_4^{2−}$/SO$_2^{−}$) = +2.5 − 3.1 V NHE [1],[2],[3]). Compared with hydroxyl radical (`OH) (E$^0$(`OH/OH$^−$) = +1.8 − 2.7 V NHE [4]), persulfate activation processes possibly outperform the conventional advanced oxidation processes (AOPs) utilizing H$_2$O$_2$ in oxidation of recalcitrant organics; selected pollutants such as perfluorinated compounds and cyanuric acid that resist `OH-induced oxidation could be degraded by SO$_4^{2−}$ [5,6]. The strategies to activate persulfate are based on the peroxide bond cleavage via energy and electron transfer processes; one-electron reduction of PMS readily takes place upon the addition of various transition metal-based reagents, leading to the conversion into SO$_4^{2−}$ (e.g., Co$^{2+} +$ HSO$_5$ → Co$^{3+} +$ SO$_4^{2−}$ + OH$^−$) [7,8]. Ferrous ion, electrochemically supplied from the sacrificial iron anode, can serve as a persulfate activator and a precursor of iron-based coagulants to effectively remove persistent organics (e.g., pentachlorophenol) [9,10]. Persulfate activation can be also initiated by γ-irradiolysis [11], sonolysis [12], and electrolysis [13]. Since the homolytic scission of the PDS peroxide bond proceeds with elevating temperature above ca. 30°C [14], microwave radiation initiates SO$_4^{2−}$-induced oxidation of organics in the presence of PDS [15]. The delivery of photon energy also enables persulfate activation; UV-C enables a direct photolysis of persulfate into SO$_4^{2−}$ [16] and semiconductor photocatalysts (e.g., TiO$_2$ [17], carbon nitride [18]) are photo-excited by UV-A or visible light to initiate persulfate reduction via conduction band (CB) electron transfer that leads to peroxide bond breakdown and subsequent SO$_4^{2−}$ production.

Due to the lack of visible light reactivity, versatile and oxidative transformation reactions of organic and inorganic pollutants by TiO$_2$ are performed only with UV light. On the other hand, the use of adequate ligands forming surface charge-transfer (CT) complexes on TiO$_2$ enables the redox reactions even under visible light irradiation; hydroxyl or carboxyl functional groups of selected compounds (e.g., phenol [19], EDTA [20], fullerol [21], and glucose [22]) undergo condensation reactions with surface functional groups on TiO$_2$ generating the visible-light-active CT complexes with the release of water molecules. The metal–ligand charge transfer (MLCT) process in which the excited CT complexes inject electrons to the CB of TiO$_2$ allows the reductive treatment of some pollutants (e.g., CCl$_4$, Cr(VI)) and production of hydrogen gas from water under visible light irradiation [23]. In particular, the electrons originated from the CT complexes are exploitable for the reduction of radical precursors such as O$_2$ and H$_2$O$_2$, which likely leads to production of reactive oxygen species (ROS) and subsequent destruction of organic compounds [23]. This may lead us to consider the MLCT mechanism for activating persulfate via one-electron reduction under visible light illumination.

H$_2$O$_2$ forms a visible-light-responsive CT complex on TiO$_2$ through the condensation reaction (i.e., > Ti-OH + H$_2$O$_2$ → > Ti-OOH + H$_2$O) based on the FT-IR absorption band characteristic of surface hydroperoxo group (i.e., Ti-µ-peroxide; Ti-OOH) in the range of 740–800 cm$^{−1}$ [24]. The surface complexation extends the absorption and photo-response of TiO$_2$ up to 550 nm [23]. When exciting the CT complex with visible light, surface-bound Ti-peroxo radical forms as a short-lived oxidation intermediate with injecting an electron to TiO$_2$ CB (Eq. (1)). The peroxy radical further decomposes into tianol group and oxygen molecule (Eq. (2)), and the transferred electron reductively cleaves surface-absorbed H$_2$O$_2$ into `OH (Eq. (3)).

\[
\begin{align*}
> \text{Ti-OH} + \text{H}_2\text{O}_2 & \rightarrow > \text{Ti-OOH} + \text{H}_2\text{O} \quad (1) \\
> \text{Ti-OOH} & \rightarrow > \text{Ti-OOH} + 1/2\text{O}_2 \quad (2) \\
\text{TiO}_2 (\text{e}^{−}) + \text{H}_2\text{O}_2 & \rightarrow \text{OH}^{−} + \text{H}_2\text{O} \quad (3)
\end{align*}
\]

Considering the aforementioned photochemistry of the TiO$_2$-H$_2$O$_2$ surface CT complex [25], PMS as a simple peroxide is likely to serve the identical dual roles as a ligand and a radical precursor when the binary mixture of TiO$_2$ and PMS is exposed to visible light (see Scheme 1); PMS contains a hydroxyl moiety to allow the surface complexation on TiO$_2$, and the electrons transferred from the visible-light-excited CT complexes possibly cause the production of PMS-derived radical (i.e., SO$_4^{2−}$).

In this study, the TiO$_2$-PMS CT complex-mediated activation of PMS (i.e., conversion of PMS to SO$_4^{2−}$) for the oxidative degradation of various organic pollutants under visible light irradiation was first hypothesized and then validated. The surface complexation was confirmed by spectroscopic characterizations. The effects of reaction parameters such as pH, PMS concentration, and irradiation wavelengths were investigated and the mechanism of PMS activation under visible light was proposed based on various experimental evidences.

2. Material and methods

2.1. Chemicals and materials

The chemicals that were used as-received in this study include the following: titanium dioxide (TiO$_2$, Degussa P25, average surface area = 50 m$^2$/g, particle size = 20–30 nm), cobalt oxide (Co$_3$O$_4$, Aldrich), acetylaminophen (Aldrich), carbamazepine (Aldrich), 4-chlorophenol (4-CP, Aldrich), furfuryl alcohol (Aldrich), nitrobenzene (Aldrich), nitrophenol (Aldrich), phenol (Junsei), sodium dichloroacetate (DCA, Aldrich), potassium peroxymonosulfate (OXONE, PMS, Aldrich), lithium perchlorate (Aldrich), sodium chloride (Aldrich), sodium fluoride (Aldrich), methanol (J.T. Baker), tert-butyl alcohol (Aldrich), HSO$_5^−$, SO$_4^{2−}$, CB, TiO$_2$, VB, H$_2$O$_2$, and PMS. The scheme proposed for PMS activation through visible light-induced charge transfer in TiO$_2$-PMS surface complex.
sodium dichromate dihydrate (Aldrich), phosphoric acid (Aldrich),
coumarin (Aldrich), 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic
acid) diamonium salt (ABTS, Aldrich), 5,5-dimethyl-1-pyrroline N-
oxide (DMPO, Tokyo Chemical Industry Co., Ltd.), sodium tetraborate
(Aldrich), potassium hydrogen phthalate (Aldrich), sodium phosphoric
monobasic (Aldrich), sodium phosphate dibasic (Aldrich), hydrochloric
acid (Samchun), sodium hydroxide (Aldrich), perchloric acid (Aldrich),
sodium bicarbonate (Kanto Chemical), sodium carbonate (Junsei),
phosphoric acid (Aldrich), and acetonitrile (J.T Baker). All chemicals
used in this study were of the highest purity available and used without
further purification. Ultrapure water (> 18 MΩ-cm) produced by a
Barnstead purification system was used to prepare all the suspensions
and solutions.

2.2. Catalyst modification and characterization

The adsorption of PMS on TiO2 surface is critically required for the
activation and it can be inhibited by adsorbing phosphate on TiO2
surface. When the effect of surface passivation by phosphate was in-
vestigated, TiO2 was modified as follows. 0.1 g TiO2 was suspended in
100 mL aqueous solution of 100 mM phosphoric acid and continuous
stirring for 5 h allowed phosphate anions to be sufficiently adsorbed on
TiO2 surface. The resultant powder (noted as P-TiO2) was dried in an
oven at 80 °C for 2 h, subjected to thermal treatment in a furnace at
300 °C for 1 h, and washed with distilled water to remove weakly-
bound phosphate anions. Electron energy loss spectroscopy (EELS)
mapping analysis was performed using a JEM-2200FS microscope with
Cs correction to confirm the uniform distribution of sulfur on the TiO2/
PMS and P-TiO2/PMS samples. The surface composition of TiO2 ad-
sorbed with PMS was investigated by X-ray photoelectron spectroscopy
(XPS, ESCALAB 250, VG Scientific) using the Al Kα line (1486.6 eV) as
an excitation source. To identify the surface functional groups on the
TiO2/PMS and P-TiO2/PMS samples, the infrared spectra were acquired
with a Thermo Scientific iS50 Fourier transform infrared (FT-IR)
spectrometer in a reflectance mode. Diffuse reflectance UV-visible
were recorded with a UV/visible spectrophotometer (Shimadzu UV-2600)
to monitor the possible red-shift of the absorption edge of TiO2/PMS in the
visible light region.

2.3. Experimental procedure and analytical methods

The photodegradation of organic compounds proceeded in a
magnetically-stirred 50 mL Pyrex reactor under air-equilibrated condi-
tion. The reactor was irradiated with a 300-W Xe-arc lamp (Oriel). The
incoming light passed through 10 cm IR filter to minimize temperature
increase during the photo-illumination, and a cut-off filter allowing
λ > 420 nm was used for visible light irradiation. Typical experi-
mental suspensions contained 0.5 g/L TiO2, 0.5 mM PMS, and 0.1 mM
target substrate, and the pH of the aqueous suspensions was adjusted to
5.0 with concentrated HClO4 or NaOH. Prior to the photo-irradia-
tion, the suspensions were agitated in the dark for 30 min in order to
make sure that the removal of organic substrate via sorption was neg-
ligible. Aliquots of 1 mL were withdrawn from the suspensions at pre-
determined time intervals, filtered through a 0.45-µm PTFE syringe
filter (Millipore), and injected to a 2-mL amber glass vial.

Residual concentrations of most organic substrates were measured
using a high performance liquid chromatography (HPLC, Agilent 1260
Infinity) equipped with a diode array detector and a ZORBAX 300SB-
C18 column (4.6 mm × 150 mm). The binary mixture consisting of
0.1% of aqueous phosphoric acid and acetonitrile (80:20 v/v) was used
as a mobile phase. Dichloroacetate (DCA) and chloride ion were
quantified with an ion chromatograph (IC, Dionex DX-120) equipped
with a Dionex Ionpac AS-14 column and a conductivity detector. The
element concentration was monitored according to modified ABTS method [26];
product formed through the one-electron oxidation of ABTS was col-
orimetrically determined at 415 nm. Hydroxylolation of coumarin
(leading to the production of 7-hydroxycoumarin) was employed as an
indirect indication of SO4
2− yield [27]; the oxidation product was
monitored by a spectrophotometer (HORIBA, Fluoromax 4C-TCSPC)
with the excitation wavelength at 332 nm and emission wavelength
monitored at 450 nm. For electron paramagnetic resonance (EPR)
analysis, 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) was employed as a
spin-trapping agent for SO4
2−. The EPR spectra was recorded for the
samples of TiO2, PMS, and the binary mixture of TiO2 and PMS using a
JES-TE 300 spectrometer (UEOL, Japan) under the following conditions:
microwave power = 3 mW, microwave frequency = 9.42 GHz, center
field = 338.25 mT, modulation width = 0.2 mT, and modulation fre-
quency = 100 kHz.

Photocurrent measurement was conducted in a conventional three-
electrode cell using a computer-controlled potentiostat (Gamry, Reference 600). The electrochemical cell magnetically stirred and
continuously purged with argon to maintain an anoxic condition. The
cell contained a TiO2-coated fluorine-doped tin oxide (FTO) glass (i.e.,
TiO2/FTO was prepared using doctor blade method as described

![Graph](image1.png)

**Fig. 1.** Oxidative degradation of 4-chlorophenol (4-CP) and dichloroacetate (DCA) in the suspension of TiO2 and PMS under visible light. P-TiO2 indicates TiO2 whose
surface is adsorbed with phosphate ions. ([TiO2]0 = 0.5 g/L; [PMS]0 = 0.5 mM; [4-CP]0 = [DCA]0 = 100 µM; pH = 5.0).
previously [28]), a Pt wire, and a Ag/AgCl (3.0 M KCl) electrode as the working, counter, and reference electrode, respectively, in 10 mM LiClO₄ electrolyte solution. For photocurrent monitoring, the working electrode was biased at an applied potential of +1.0 V (vs Ag/AgCl). A 300-W Xe-arc lamp equipped with an optical filter cutting off below 455 nm was used as a light source.

3. Results and discussion


Fig. 1 shows that 4-CP degradation significantly proceeded with the concurrent release of chloride ions (Cl⁻) in the aqueous TiO₂ suspensions containing PMS under visible light irradiation. It is noted that the generated chloride concentration was lower than the removed 4-CP concentration, which implies that the mineralization was not complete. The TOC (total organic carbon) measurement demonstrated that the chloride concentration was lower than the removed 4-CP concentration, which implies that the mineralization was not complete. The TOC (total organic carbon) measurement demonstrated that the chloride concentration was lower than the removed 4-CP concentration, which implies that the mineralization was not complete.

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3.2. Formation of visible-light-absorbing surface complex

The EELS map of TiO₂ sample obtained after 5 min exposure to aqueous PMS solution shows that sulfur atoms are uniformly distributed on the TiO₂ surface (Fig. 3f), which is in marked contrast to the EELS image of pure TiO₂ in Fig. 3c. The XPS spectrum of S 2p in the PMS-treated TiO₂ also confirms the surface sulfur species (Fig. 3h) and the surface sulfur content was estimated to be ca. 2.8%. The FT-IR absorption band associated with S-O bond stretching was found at 1199 cm⁻¹ [34] and became more pronounced when applying 10-fold higher concentration of PMS (Fig. 3g), which corroborates the possible PMS linkage to the surface of TiO₂. The IR band assignable to the stretching vibration of S-O group remained when the calcination temperature increased up to 500 °C, whereas the broad absorption band centered at 3400 cm⁻¹ [35] was detected in the IR spectrum of PMS alone. This indicates that the TiO₂/PMS surface complex is stable up to 500 °C. Whereas the hydroxyl group characterized by the broad absorption band centered at 3400 cm⁻¹ [35] was detected in the IR spectrum of PMS alone, the corresponding IR band disappeared in the spectrum of TiO₂/PMS (Fig. 3g). This supports the possibility that the hydroxyl moiety of PMS is involved in the surface chelation process (see Scheme 1). Contrary to the previous finding on visible-light-driven H₂O₂ activation via LMCT [24], we observed that 4-CP oxidation was not markedly enhanced when H₂O₂ was applied instead of PMS (Fig. S3).

The dual roles of PMS as a surface complexing agent and a radical precursor became more pronounced when DCA was used as an alternative substrate; DCA itself cannot form a CT complex with TiO₂ unlike phenolic compounds. With the stoichiometric evolution of Cl⁻, DCA completely decomposed after 4 h visible light irradiation in the aqueous TiO₂/PMS suspension (Fig. 1). Neither photolysis of PMS nor dark adsorption by the TiO₂/PMS mixture removed DCA (Fig. S2). Whereas DCA alone caused the noticeable 4-CP oxidation with visible light, DCA was not degraded at all (Fig. 1), which confirmed the inability of DCA to form a surface CT complex on TiO₂. PMS decomposition proceeded at a similar rate in the visible light-irradiated TiO₂ suspension in the presence and absence of organic substrates (Fig. S4). The results collectively rule out a possibility that surface complexation between TiO₂ and organic substrate (i.e., 4-CP) followed by the charge transfer under visible light irradiation is responsible for the reductive conversion of PMS to SO₄²⁻. This indicates the possible involvement of a surface CT complex between PMS and TiO₂ in the LMCT mechanism (note that H₂O₂ as a simple peroxide forms visible light responsive complex on TiO₂ surface [25]). TiO₂ adsorbed with phosphate ions (noted as P-TiO₂) drastically retarded the degradation of both target substrate (i.e., 4-CP and DCA) and PMS decomposition in the TiO₂/PMS/visible light system (Figs. 1 and S4). Phosphates are well known to be strongly anchored onto TiO₂ surface to hinder the adsorption of other substrates [30]. This result also assures the role of PMS as the surface complexing ligand.

The TiO₂/PMS system was examined for the oxidative degradation of various organic pollutants including acetaminophen, benzoic acid, carbamazepine, furfuryl alcohol, nitrobenzene, nitrophenol, and phenol (Fig. 2). Degradation efficiency depends on the type of substrate. Benzoic acid and carbamazepine were rapidly decomposed, and acetaminophen, nitrobenzene, and phenol were degraded at moderate rates, while nitrophenol and furfuryl alcohol underwent relatively slow decay. The performance of TiO₂/PMS in oxidative degradation appears to rely on the oxidizing capacity of SO₄²⁻ rather than the coordination capability of the organic substrate as a ligand. For example, nitrophenol that should form a surface CT complex on TiO₂ through the phenolic functional group was actually less degraded than carbamazepine and nitrobenzene (Fig. 2). On the other hand, organic substrates that were more susceptible to oxidation on TiO₂/PMS exhibit higher reactivity toward SO₄²⁻; benzoic acid rapidly reacts with SO₄²⁻ (k (benzoic acid + SO₄²⁻) = 1.2 × 10⁹ M⁻¹ s⁻¹) whereas nitrobenzene is much less reactive toward SO₄²⁻ (k (nitrobenzene + SO₄²⁻) < 10⁸ M⁻¹ s⁻¹) [31]. Photochemically- or thermally-activated persulfate was demonstrated to effectively degrade carbamazepine [32,33].

\[
> \text{Ti-OH} + \text{HSO}_5^- \rightarrow > \text{Ti-OOSO}_3^- + \text{H}_2\text{O}
\]  

(4)
Diffuse reflectance measurement demonstrates that the TiO$_2$/PMS mixture produced a broad absorption tail that extends up to 500 nm whereas visible light absorption band did not appear at all in the spectrum of pure TiO$_2$ (Fig. 4). This implies the formation of a visible-light-absorbing surface complex involving PMS. Fig. 4 shows the photosensitizing activity of TiO$_2$/PMS for the oxidative degradation of 4-CP and DCA under different wavelengths of visible light irradiation, which were controlled using a suite of optical filters cutting off below the specific wavelengths. The photosensitized oxidation was retarded with increasing the cut-off wavelength, with $k_{\text{DCA}} = 0.549 \text{h}^{-1}$ under $\lambda > 420 \text{nm}$ and $k_{\text{DCA}} = 0.167 \text{h}^{-1}$ under $\lambda > 455 \text{nm}$, was significantly hindered under $\lambda > 550 \text{nm}$ and negligible under $\lambda > 645 \text{nm}$. The wavelength-dependent photosensitizing activity of TiO$_2$/PMS correlates well with its UV–visible absorption spectrum (Fig. 4), which suggests that the surface CT complex should be responsible for visible-light-induced oxidation in the TiO$_2$/PMS suspensions.

3.3. Effects of reaction parameters

We monitored the 4-CP degradation kinetics in the TiO$_2$/PMS suspensions with increasing PMS dosage (Fig. 5a). 4-CP decay was gradually accelerated as initial PMS concentration increased up to 0.5 mM above which the further increase of [PMS] was not effective. It is noteworthy that the IR peak assigned to S–O band and visible absorption band in the DRS became more intense when increasing the initial PMS concentration from 10 mM to 100 mM (Figs. 3g and 4). This reveals that the PMS level that causes the complete TiO$_2$ surface coverage through the complexation should be much higher than the PMS level (0.5–5 mM) that maximizes the photosensitizing activity of TiO$_2$/PMS. No further kinetic enhancement in 4-CP degradation at [PMS] > 0.5 mM may be attributed to the competition between PMS and 4-CP for $\text{SO}_4^{2-}$ rather than TiO$_2$ surface saturation. PMS that is highly concentrated on TiO$_2$ surface should readily consume $\text{SO}_4^{2-}$ even if the rate constant for the oxidation of PMS by $\text{SO}_4^{2-}$ is not significant ($k_{\text{(PMS + SO}_4^{2-})} < 10^5 \text{M}^{-1}\text{s}^{-1}$) [36].
which are compared with the rate constant of the degradation of 4-CP by TiO₂/PMS for the degradation of organic substrates ([TiO₂]₀ = 0.5 g/L; [4-CP]₀ = 100 µM; [PMS]₀ = 0.5 mM; [DCA]₀ = 100 µM). The dotted lines indicate the transmittance profiles of the cut-off filters.

Fig. 5. Effects of (a) initial PMS concentration and (b) pH on the activity of TiO₂/PMS for the degradation of organic substrates ([TiO₂]₀ = 0.5 g/L; [4-CP]₀ = [DCA]₀ = 100 µM).

Fig. 5b shows the pH-dependent efficiencies of the TiO₂/PMS system for degradation of 4-CP and DCA. Different pH effects were observed; 4-CP oxidation decreased with increasing pH whereas weakly acidic and neutral pH condition favored DCA degradation. PMS exists as an anion over a wide pH range (i.e., pKa₁ = 4.0 and pKa₂ = 9.3) [37,38], and the TiO₂ surface is positively and negatively charged in acidic and basic condition, respectively (pH of the point of zero charge = 6.3) [39]. Accordingly, 4-CP and DCA decay was kinetically retarded at basic pH where surface complexation of PMS is likely inhibited due to the electrostatic repulsion between PMS and TiO₂. Since the electrostatic attraction at acidic pH facilitates the formation of the CT complex of PMS on TiO₂ surface, the organic destruction is likely to be more rapid at pH 3 as observed in the case of 4-CP degradation. However, DCA oxidation was retarded at pH 3.0, which might be attributable to the competition of DCA and PMS anions for the positively-charged TiO₂ surface sites.

3.4. Effects of anions

Fig. 1 showed no visible light activity of P-TiO₂ for oxidative degradation of 4-CP, which was presumably due to the inhibitory effect of surface-bound phosphate on the formation of TiO₂/PMS CT complex. To further identify the role of phosphate as a protective agent, surface chemical composition of P-TiO₂ after exposure to excess PMS was analyzed; no appearance of the FT-IR band assignable to surface S-O group (Fig. S6a) and no detection of sulfur element on P-TiO₂ in the EELS image (Fig. S6i) indicate the inability of P-TiO₂ to form the surface complex with PMS. UV-visible diffuse reflectance spectrum of P-TiO₂/PMS ensured that PMS addition did not extend the absorption of P-TiO₂ into visible light region (Fig. S6b). A comparison among different anion-modified TiO₂ samples (i.e., fluoride, iodate, sulfate, perchlorate, and phosphate) were prepared according to the procedure described in the Section 2.2) for the PMS adsorption capacity showed that P-TiO₂ barely removed PMS via sorption mechanism whereas other anions-modified TiO₂ caused a noticeable sorption of PMS concentration in the dark (Fig. S7). This corroborated that surface-adsorbed phosphates effectively hindered PMS sorption and its surface complexation on TiO₂. The influence of naturally-occurring anions (i.e., Cl⁻, sulfate (SO₄²⁻), and bicarbonate (HCO₃⁻)) on the LMCT-mediated oxidation on TiO₂/PMS was also investigated by monitoring 4-CP degradation kinetics in the presence of each anion. Regardless of the anion type, 4-CP decomposition by TiO₂/PMS was not kinetically retarded in the presence of 1 mM anions (Cl⁻, SO₄²⁻, and HCO₃⁻, respectively), which likely rules out the possibility of competition between background anions and PMS for surface complexation sites on TiO₂ (data not shown).

3.5. Role of SO₄²⁻ as the main oxidant

To identify the primary degradative pathway induced by visible-light-irradiated TiO₂/PMS, the effects of two radical quenchers, methanol (MeOH) and tert-butyl alcohol (t-BuOH) were explored (Fig. 6a). The addition of excess MeOH completely inhibited DCA degradation and markedly retarded the degradation of 4-CP. These results suggest the involvement of SO₄²⁻ in oxidative degradation associated with the CT complex-mediated PMS activation. 4-CP was still degraded to a certain extent even in the presence of excess MeOH, which implies the alternative reaction route involving no SO₄²⁻; TiO₂-4CP CT complexes mediated the self-sensitized degradation of 4-CP (i.e., (TiO₂-4CP complex) → 4-CP* + TiO₂(e⁻)). Note that one-electron oxidation via the LMCT mechanism is kinetically enhanced in the presence of electron acceptors such as PMS and Cr(VI) (Fig. S8). The apparent quenching effect of t-BuOH may raise the possibility of OH-induced oxidation since t-BuOH reacts selectively with OH (k₂(t-BuOH + OH) = 3.8 × 10⁷ M⁻¹ s⁻¹ versus k₃(t-tBuOH + SO₄²⁻) = 4 × 10¹² M⁻¹ s⁻¹) [40]. However, this is likely attributed to the competition between PMS and t-BuOH for sorption sites onto TiO₂/PMS degradation efficiency in the TiO₂/PMS suspension was...
not reduced at all in the presence of MeOH whereas PMS decomposition was significantly decelerated upon t-BuOH addition (Fig. 6a).

To further confirm the role of SO$_4^{−}$ in the TiO$_2$/PMS system, we monitored the hydroxylation of coumarin as an indirect indicator for radical production in the visible-light-irradiated TiO$_2$/PMS (Fig. 6b), which is based on the findings that the attack of SO$_4^{−}$ on aromatics led to the formation of hydroxylated compounds as the major products [41]. Note that the similarity in the distribution of transient intermediates during coumarin oxidation allows us to use ‘OH measurement methods for quantitatively monitoring SO$_4^{−}$ (42,43). Whereas the formation of 7-hydroxycoumarin was almost absent with PMS or TiO$_2$ alone, the hydroxylated product concentration linearly increased with the irradiation time in the TiO$_2$/PMS suspension. The coumarin hydroxylation considerably decreased in the presence of MeOH as a SO$_4^{−}$ scavenger. In particular, it is interesting to note that the retarding effect was more pronounced with t-BuOH that is a poor scavenger of SO$_4^{−}$ [7,44,45]. This seems to imply that the presence of t-BuOH hinders the adsorption of PMS on TiO$_2$ sites. Furthermore, DMPO-SO$_4^{−}$ adduct was detected only in the EPR spectrum of TiO$_2$/PMS whereas neither PMS nor TiO$_2$ alone produced the peak pattern characteristic of SO$_4^{−}$ in the presence of DMPO as a spin-trapping agent (Fig. 6c). It is clear that the generation of SO$_4^{−}$ should be induced by the photoexcitation of the surface complex of PMS on TiO$_2$.

3.6. Activation mechanisms and processes

According to some spectroscopic evidences (Figs. 3g, h, and 4), PMS adsorption is likely to produce a visible-light-absorbing complex at TiO$_2$ surface (i.e., > Ti-OH + HSO$_5^{−}$ → > Ti-OOSO$_3^{−}$ + H$_2$O). The visible-light-induced LMCT leads to electron injection into the CB of TiO$_2$ (Eq. (5)).

$$> \text{Ti-OOSO}_3^{−} + \text{h}v \rightarrow > \text{Ti}−\text{OOSO}_3 + \text{TiO}_2^{(e^{−})}$$

(5)

$$\text{TiO}_2^{(e^{−})} + \text{HSO}_5^{−} \rightarrow \text{SO}_4^{−}^{−} + ^{•}\text{OH}$$

(6)

A direct evidence for the visible light-induced LMCT was obtained by comparing the photocurrent generated on TiO$_2$ electrode under visible light with and without PMS. PMS addition induced a significant current generation at TiO$_2$ electrode under visible light irradiation, but little photocurrent generation was observed in the absence of PMS (Fig. 7). This confirmed the direct electron transfer from the visible-light-excited surface complex (PMS/TiO$_2$) to the CB of TiO$_2$. In this event, PMS coordinated to the Ti-surface site acts as an electron donor and another PMS readily undergoes reductive conversion into SO$_4^{−}$ by electrons transferred via LMCT (Eq. (6)). Phenolic compounds that form CT complexes at TiO$_2$ surface may provide an additional reaction pathway for one-electron reduction of PMS. However, the effective degradation of organic substrates (e.g., DCA, carbamazepine) still proceeds on TiO$_2$ in the presence of PMS even though their roles as complexing agents are not significant, which assures that twofold actions of PMS as a ligand of the CT complexation and as a precursor of SO$_4^{−}$ are critical in the visible-light sensitized oxidation of organics. PMS radical (SO$_4^{−}$) may form during LMCT subsequent to the excitation of the interfacial CT complex. Based on the previous finding that the recombination of SO$_4^{−}$ caused rapid SO$_4^{−}$ generation (i.e., SO$_5^{−}$ + SO$_5^{−}$ → SO$_4^{−}$ + SO$_4^{−}$ + O$_2$; $k = 2.2 \times 10^6 \text{M}^{−1}\text{s}^{−1}$) [36], this collateral reaction route would contribute to the overall efficiency of SO$_4^{−}$ production.

We compared TiO$_2$/PMS/visible light versus Co$_3$O$_4$/PMS (a

Fig. 7. Photocurrent generation at TiO$_2$ electrode in the absence and presence of PMS ([PMS]$_0 = 0.5 \text{ mM}$; [LiClO$_4$]$_0 = 10 \text{ mM}$; pH$_1 = 5.0$).
benchmark system to produce $\text{SO}_4^{2-}$ in the dark) in terms of the repeated oxidation of acetaminophen (Fig. 5). Catalytic performance of activators (i.e., TiO$_2$ and Co$_3$O$_4$) was examined in the same batch with fresh PMS supplied in each cycle. The use of Co$_3$O$_4$ as a PMS activator led to gradual reduction in organic degradation efficiency. In contrast, TiO$_2$/PMS exhibited constant activity for acetaminophen oxidation repeated uses. In contrast, TiO$_2$ that provides a metallic coordination surface of TiO$_2$. Visible-light-driven production of SO$_4^{2-}$ can repeatedly proceed on TiO$_2$ as long as persulfate is sufficiently supplied. The persulfate activation on TiO$_2$ via LMCT is advantageous since it needs low photon energy and durable and low-cost catalyst.

4. Conclusions

This study demonstrated the first instance of visible-light-induced oxidation of organic pollutants via a TiO$_2$/PMS CT complex. Unlike the conventional photochemical activation methods to excite either PMS or TiO$_2$ with UV light, the dual roles of PMS as a surface complexing ligand and a radical precursor allow visible light (or natural sunlight) to activate PMS on TiO$_2$. Several spectroscopic analyses confirmed the surface complexation of TiO$_2$ with PMS through the condensation reaction, and the absorption spectrum of TiO$_2$/PMS in the visible light region is consistent with the wavelength-dependent degradation of 4-CP. Visible-light-driven production of SO$_4^{2-}$ was supported by the following results: significant quenching effect of methanol, effective coumarin hydroxylation, EPR spectral features corresponding to the radical adduct, and substrate-specific treatment efficiency that matched the reactivity of SO$_4^{2-}$. Since the net reaction for PMS activation on TiO$_2$ is electron exchange between two PMS molecules (i.e., electron transfer from PMS as a complexing agent to another PMS as a SO$_4^{2-}$ precursor: Eq. (5) + Eq. (6)), the oxidative degradation of organic pollutants can repeatedly proceed on TiO$_2$ as long as persulfate is sufficiently supplied. The persulfate activation on TiO$_2$ via LMCT is advantageous since it needs low photon energy and durable and low-cost catalyst.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cej.2018.03.150.

References


