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# Activation of peroxymonosulfate on visible light irradiated $TiO_2$ via a charge transfer complex path

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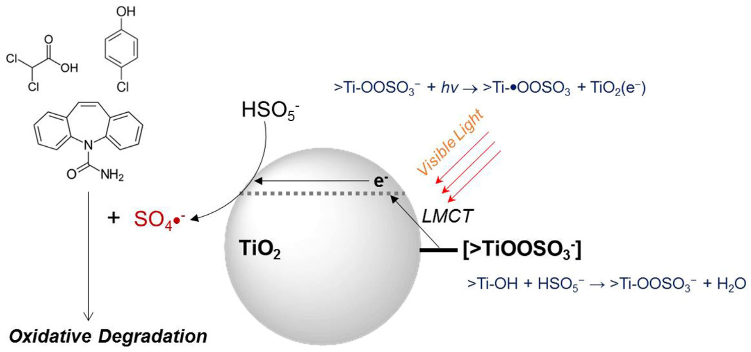
## HIGHLIGHTS

- 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.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

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## 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 ($SO_4^{\cdot -}$) 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 $SO_4^{\cdot -}$. 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 $SO_4^{\cdot -}$. 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 $SO_4^{\cdot -}$ as the main oxidant was identified based on (1) quenching effect of methanol as a radical quencher, (2) coumarin

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hydroxylation as an indication of $SO_4^{\cdot-}$ formation, and (3) EPR spin-trapping technique. The comparison of $TiO_2$/PMS *versus* $Co_3O_4$/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 $Co_3O_4$/PMS.

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## 1. Introduction

Persulfate (collectively representing peroxymonosulfate (PMS; $HSO_5^-$) and peroxydisulfate (PDS; $S_2O_8^{2-}$)) activation has been demonstrated to rapidly degrade a wide range of organic pollutants possessing different chemical structures through the production of sulfate radical ($SO_4^{\cdot-}$) as a highly reactive intermediate ($E^0(SO_4^{\cdot-}/SO_4^{2-}) = +2.5 - 3.1\ V_{NHE}$ [1]) [2,3]. Compared with hydroxyl radical ($^\cdot OH$) ($E^0(^\cdot OH/OH^-) = +1.8 - 2.7\ V_{NHE}$ [4]), persulfate activation processes possibly outperform the conventional advanced oxidation processes (AOPs) utilizing $H_2O_2$ in oxidation of recalcitrant organics; selected pollutants such as perfluorinated compounds and cyanuric acid that resist $^\cdot OH$-induced oxidation could be degraded by $SO_4^{\cdot-}$ [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 $SO_4^{\cdot-}$ (*e.g.*, $Co^{2+} + HSO_5^- \rightarrow Co^{3+} + SO_4^{\cdot-} + OH^-$) [7,8]. Ferrous ion, electrochemically supplied from the sacrificial iron anode, can serve as a persulfate activator and a precursor of iron-based coagulant to effectively remove persistent organics (*e.g.*, pentachlorophenol) [9,10]. Persulfate activation can be also initiated by γ-radiolysis [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 $SO_4^{\cdot-}$ -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 $SO_4^{\cdot-}$ [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 $SO_4^{\cdot-}$ production.

Due to the lack of visible light responsivity, reductive 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 hydroxyl 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 $H_2O_2$, 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.

$H_2O_2$ forms a visible-light-responsive CT complex on $TiO_2$ through the condensation reaction (*i.e.*, $>\text{Ti-OH} + H_2O_2 \rightarrow\ >\text{Ti-OOH} + H_2O$) 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 peroxo radical further decomposes into tianol group and oxygen molecule (Eq. (2)), and the transferred electron reductively cleaves surface-absorbed $H_2O_2$ into $^\cdot OH$ (Eq. (3)).

$$>\text{Ti-OOH} + h\nu \rightarrow\ >\text{Ti-}{\cdot}\text{OOH} + TiO_2\ (e^-) \tag{1}$$

$$>\text{Ti-}{\cdot}\text{OOH} \rightarrow\ >\text{Ti-OH} + 1/2O_2 \tag{2}$$

$$TiO_2\ (e^-) + H_2O_2 \rightarrow {}^\cdot OH + {}^-OH \tag{3}$$

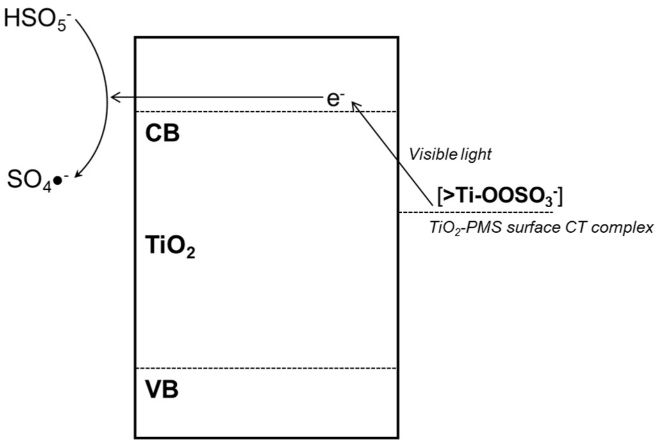
Considering the aforementioned photochemistry of the $TiO_2$-$H_2O_2$ surface CT complex [25], PMS as a simple peroxide is likely to serve the identical dual roles as a ligand and a radical precursor when the binary mixture of $TiO_2$ and PMS is exposed to visible light (*see* Scheme 1); PMS contains 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.*, $SO_4^{\cdot-}$).

In this study, the $TiO_2$-PMS CT complex-mediated activation of PMS (*i.e.*, conversion of PMS to $SO_4^{\cdot-}$) 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 ($Co_3O_4$, Aldrich), acetaminophen (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 sulfate (Aldrich), iodic acid (Aldrich), sodium fluoride (Aldrich), methanol (J.T. Baker), *tert*-butyl alcohol (Aldrich),



**Scheme 1.** Proposed mechanism for PMS activation through visible light-induced charge transfer in $TiO_2$-PMS surface complex.