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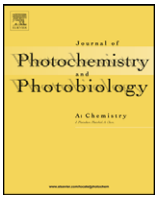

# Characterization of the hydroperoxyl/superoxide anion radical ($HO_2^{\bullet}/O_2^{\bullet-}$) formed from the photolysis of immobilized $TiO_2$ in a continuous flow

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ABSTRACT

In this study, the steady-state concentrations of $HO_2^{\bullet}/O_2^{\bullet-}$ formed from the photocatalysis of immobilized $TiO_2$ were investigated quantitatively by using the kinetic method with a continuous flow injection. In air-equilibrated water, the concentration of $HO_2^{\bullet}/O_2^{\bullet-}$ was typically 1.01 (±0.08) × $10^{-9}$ M at pH 5.80 in the absence of buffers. The reduction of $O_2$ by photo-induced electrons ($e_{cb}^-$) was increased by the concentration of $O_2$ (from 0 to 0.38 mM). However, in the presence of buffer anions the concentration of $HO_2^{\bullet}/O_2^{\bullet-}$ was gradually decreased by increasing pH. This indicates that the suppression of $HO_2^{\bullet}/O_2^{\bullet-}$ in the presence of buffer ions is attributed to the blocking of active sites of the immobilized $TiO_2$ photocatalyst and to certain processes, that is, the reaction between $HO_2^{\bullet}/O_2^{\bullet-}$ and $^{\bullet}OH$ (and/or $h_{vb}^+$). Furthermore, the concentration of $HO_2^{\bullet}/O_2^{\bullet-}$ increased with the increasing concentrations of $H_2O_2$ and oxalate, and then on the further addition of $H_2O_2$ (>10 mM) and oxalate (>2 mM), the concentration of $HO_2^{\bullet}/O_2^{\bullet-}$ reached steady values. These results strongly suggest that $HO_2^{\bullet}/O_2^{\bullet-}$ formed on $TiO_2$ photocatalysis migrates into the water bulk, and this study can contribute significantly to the body of knowledge regarding $HO_2^{\bullet}/O_2^{\bullet-}$ at very low levels.

## 1. Introduction

Photocatalytic applications of $TiO_2$ have been of major interest in the area of wastewater treatment, especially when the wastewater contains a wide variety of undesirable pollutants [1–3]. In the previous studies of the $TiO_2$ photolysis, reactive intermediates such as the hydroxyl radical ($^{\bullet}OH$) [4–13], the hydroperoxyl/superoxide anion radical ($HO_2^{\bullet}/O_2^{\bullet-}$) [12–22], singlet oxygen ($^1O_2$) [17–22], and hydrogen peroxide ($H_2O_2$) [15,20] have been identified and their formation mechanisms have also been proposed. While the hydroxyl radicals produced on hydrated $TiO_2$ particles are fairly well investigated in a series of degradation reactions with pollutant molecules [4–13,23,24], much less attention has been paid to the role of $HO_2^{\bullet}/O_2^{\bullet-}$. Recently, several studies have paid much more attention to the behaviors of $HO_2^{\bullet}/O_2^{\bullet-}$ produced through the electron transfer from the $TiO_2$ surface to dissolved oxygen ($O_2$), since the formation of $HO_2^{\bullet}/O_2^{\bullet-}$ is important process to determine the efficiency of $TiO_2$ photocatalytic reactions by means of the decrease of electron–hole ($e^-$–$h^+$) recombination [15,16,24]. In view of this point, the physicochemical features on $HO_2^{\bullet}/O_2^{\bullet-}$ formation, i.e., migrated (or drift) $HO_2^{\bullet}/O_2^{\bullet-}$, are very important to explore the $TiO_2$ photocatalytic activity. In addition, a large amount of attention has been focused on the potential role of $HO_2^{\bullet}/O_2^{\bullet-}$ in eliminating various pollutants in water including atrazine, phenols, and chlorophenol [25–29]. Nevertheless, further investigated is warranted concerning the generation and deactivation of $HO_2^{\bullet}/O_2^{\bullet-}$, as well, quantitative information is needed [15–17,19,24].

Although a number of studies have been conducted to investigate $HO_2^{\bullet}/O_2^{\bullet-}$ formation in the $TiO_2$ photolysis, the basic mechanism is considered to represent the best reaction model for explaining the fate of $HO_2^{\bullet}/O_2^{\bullet-}$ in an aqueous phase as follows [12,16,30–35]:

$$TiO_2 + h\upsilon(< 400\,\text{nm}) \rightarrow h_{vb}^+ + e_{cb}^- \tag{I}$$

$$H_2O\,(\text{or}OH^-) + h_{vb}^+ \rightarrow {}^{\bullet}OH + H^+ \tag{II}$$

$$O_2 + e_{cb}^- \rightarrow O_2^{\bullet-} \tag{III}$$

$$O_2^{\bullet-} + H^+ \leftrightarrow HO_2^{\bullet} \tag{IV}$$

$$O_2^{\bullet-} + h_{vb}^+ \rightarrow O_2 \tag{V}$$

In the aqueous phase, the photolysis of $TiO_2$ leads to the formation of a valence band hole ($h_{vb}^+$) and a conduction band electron ($e_{cb}^-$) in reaction (I). The hydroxyl radical ($^{\bullet}OH$) is produced from $H_2O$ (or

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$OH^-$) on the hydrated $TiO_2$ surface by trapping an $h_{vb}^+$ (reaction (II)). Subsequently, the oxygen molecules adsorbed on the surface of air-saturated $TiO_2$ act as electron scavengers and combine with $e_{cb}^-$ to form $O_2^{\bullet-}$ in the reaction (III), which is in an acid–base equilibrium (reaction (VI); p$K_a$ ($HO_2^\bullet$) = 4.8 ± 0.1) [36]. The reduction of $O_2$ by $e_{cb}^-$ (reaction (III)) can exclude the accumulation of the electrons on the $TiO_2$ particles as well as $e^-$–$h^+$ recombination. However, $h_{vb}^+$ remaining on the $TiO_2$ surface is reported to eliminate $O_2^{\bullet-}$ (reaction (V)) [32,33]. Thus, the formation of $HO_2^\bullet/O_2^{\bullet-}$ has been considered as an intermediate of the ensuing reactions of free radicals in air-saturated water during the photolysis of $TiO_2$.

Thus far, several methods have been developed for the detection of $HO_2^\bullet/O_2^{\bullet-}$ formed in illuminated $TiO_2$ suspensions. For an examination of active species produced on $TiO_2$ surfaces, the electron paramagnetic resonance (EPR) technique has been most commonly used at a very low temperature or at room temperature [5,12,37,38]. However, the EPR technique has only focused on the detection of $HO_2^\bullet/O_2^{\bullet-}$, rather than on the determination of the absolute concentration of $HO_2^\bullet/O_2^{\bullet-}$. Nosaka et al. [14,15] and Hirakawa et al. [24,33] have recently developed a chemiluminescence (CL) method to detect reactive oxygen species formed on a $TiO_2$ photocatalyst. They dropped luminol as a specific probe on a $TiO_2$ aqueous suspension or on $TiO_2$ film. However, this method has a shortcoming, in that reactions with various reactive oxygen species without the separation of $HO_2^\bullet/O_2^{\bullet-}$ occur; thus only an estimated (or calculated) concentration of $HO_2^\bullet/O_2^{\bullet-}$ is reported. In contrast, Ishibashi et al. [16,19] applied this method using luminol or MCLA (2-methyl-6-(*p*-methoxyphenyl)-3,7-dihydroimidazo-[1,2-*a*]pyrazin-3-one) as a specific probe to $TiO_2$ film-type photocatalysts in air and in water. To determine the absolute number of $O_2^{\bullet-}$, the photon emission standards were measured from the luminol oxidation initiated with the addition of 0.1% hydrogen peroxide in a standard cell, and the quantitative number of $O_2^{\bullet-}$ was then estimated by comparing the photon number from the standard photon emission of luminol with that emitted from the reaction between photo-generated $O_2^{\bullet-}$ and luminol [19]. However, there are issues with an interfering effect such as $H_2O_2$-induced CL in the presence of metal and additionally required experimental such as a standard photon emission. Other issues involve the selectivity of luminol from various reactive oxygen species during $TiO_2$ photolysis [15,19,24,33]. Interestingly, no such steady-state concentration of $HO_2^\bullet/O_2^{\bullet-}$ formed at continuous flow injection has been reported to the best of my knowledge. Thus, information regarding the concentration of $HO_2^\bullet/O_2^{\bullet-}$ has been limited in previous studies involving the photolysis of $TiO_2$.

For an alternative method of determining the $HO_2^\bullet/O_2^{\bullet-}$ concentration, Kwon et al. [39,40] developed a kinetic method for the measurement of $HO_2^\bullet/O_2^{\bullet-}$ in an aqueous solution. In this method, a calibration procedure using a kinetic half-life technique is established for determining the concentration of $HO_2^\bullet/O_2^{\bullet-}$ as produced in the UV/$H_2O_2$ process. The kinetic method has shown high sensitivity with a simple calibration system.

In this study, the steady-state concentration of $HO_2^\bullet/O_2^{\bullet-}$ in an illuminated $TiO_2$ film using the kinetic method is quantitatively determined. To investigate the generation and deactivation of $HO_2^\bullet/O_2^{\bullet-}$ in the photolysis of $TiO_2$, various effects of the pH using anion buffers, dissolved oxygen, and wavelengths are examined. In addition, the effects of hydrogen peroxide and oxalate are examined in the $TiO_2$ photolysis. In particular, this study is the first report of utilizing the continuous flow injection in the investigation of $TiO_2$ photocatalytic reactions on the generation and deactivation of $HO_2^\bullet/O_2^{\bullet-}$ to my knowledge.

## 2. Experimental

### 2.1. Materials

Anatase $TiO_2$ (particle size-325 mesh, 99+%) was obtained from Aldrich. Ferric ethylenediaminetetra acetate ($Fe^{3+}$-EDTA), sulfuric acid, sodium hydroxide, benzoic acid (BA), sodium oxalate, and 3% $H_2O_2$ were of reagent grade and were purchased from Sigma–Aldrich. The solution pH was adjusted to the ranges between 5 and 9.5 with a phosphate buffer (Sigma) and a borate buffer (LabChem Inc.) in addition to $H_2SO_4$ and NaOH. The concentration of the $H_2O_2$ stock solution was determined through the use of a $KMnO_4$ titration method prior to use. The working $H_2O_2$ solution was prepared daily by diluting the $H_2O_2$ stock solution with the proper level with high-purity deionized (DI) water. $O_2$ saturation in the DI water was achieved by purging high purity $O_2$ gas (≥99.995%) to dissolve molecular oxygen, and $N_2$ saturation in the DI water was achieved through the use of high purity $N_2$ gas (≥99.99%) to remove molecular oxygen. All other chemicals were of analytical grade and were used as received. All solutions were made with high-purity (>18 MΩ cm) DI water from the Younglin ultra-purification system (Korea).

### 2.2. Preparation of the $TiO_2$-coated quartz coil

$TiO_2$ particles were immobilized on the inner surface of a quartz coil (i.d. 1 mm × length 900 mm; inner surface **area ≈2800 $mm^2$). The quartz coil was pre-cleaned with 1% nitric acid and washed with pumped DI water by pumping for 2 h at 1.00 mL/min. Two hundred micrograms of $TiO_2$ was added into 3 mL methanol, and this was stirred with a magnetic stirrer. 0.3 mL $TiO_2$ suspension was gradually poured into the quartz coil and it was dried at 40 °C. This process was repeated 10 times to achieve an even coating. This coil was subsequently calcined in a furnace at 600 °C for 3 h [41]. Following this, the quartz coil with the immobilized $TiO_2$ particles was cooled to room temperature in air. X-ray diffraction (XRD) was used to analyze the change of crystalline structure of $TiO_2$. Anatase and rutile $TiO_2$ were both present in the calcined powders, but the main structure was anatase (data not shown).

### 2.3. $HO_2^\bullet/O_2^{\bullet-}$ determination in the photolysis of $TiO_2$

A schematic diagram for the $HO_2^\bullet/O_2^{\bullet-}$ measurement system is shown in Fig. 1. The apparatus and the experimental procedures employed in this study are similar to those of a previous study [39,40] except the $TiO_2$ particles immobilized on the quartz coil. All solutions were delivered using a peristaltic pump (Ismatec, type ISM 946) with PTFE tubing (Cole-Parmer, i.d. 1.07 mm).

During the measurement of $HO_2^\bullet/O_2^{\bullet-}$, DI water was delivered through Port 1 (P1, 0.43 mL/min) with Valve 1 (V1) opened, while Valve 2 (V2) and Valve 3 (V3) were closed. Dissolved oxygen (DO) in the DI water led to the formation of $HO_2^\bullet/O_2^{\bullet-}$ in the $TiO_2$-coated quartz coil illuminated with a 4-W low pressure Hg lamp (Sankyo Denki Co., Japan). $H_2O_2$ was added through Port 2 (P2, 0.23 mL/min) and was mixed with a premixed solution containing $Fe^{3+}$-EDTA (P3, 0.23 mL/min) and BA (P4, 0.23 mL/min). The $Fe^{3+}$-EDTA was reduced by $HO_2^\bullet/O_2^{\bullet-}$ to $Fe^{2+}$-EDTA with $k_6 = 2 \times 10^6\ M^{-1}\ s^{-1}$.

$$Fe^{3+}\text{-EDTA} + O_2^{\bullet-}\,(HO_2^\bullet) \rightarrow Fe^{2+}\text{-EDTA} + O_2(+H^+) \qquad (VI)$$

A subsequent Fenton-like reaction between $Fe^{2+}$-EDTA and $H_2O_2$ ($k_7 = (2 \pm 1) \times 10^4\ M^{-1}\ s^{-1}$) led to the production of the $^\bullet OH$ radicals and to the regeneration of $Fe^{3+}$-EDTA.

$$Fe^{2+}\text{-EDTA} + H_2O_2 \rightarrow Fe^{3+}\text{-EDTA} + OH^- + {}^\bullet OH \qquad (VII)$$