Experimental Evidence of the Mobility of Hydroperoxyl/Superoxide Anion Radicals from the Illuminated TiO$_2$ Interface into the Aqueous Phase

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The understanding of behaviors of hydroperoxyl/superoxide anion radicals (HO$_2$·/O$_2$·) generated from a photo-irradiated TiO$_2$ surface is essential to improve the efficiency of TiO$_2$ photocatalytic reactions by decreasing the recombination of photoinduced electron-hole (e$^-$-h$^+$) pairs. In contrast with previous studies, we found that HO$_2$·/O$_2$· generated on the surface of illuminated TiO$_2$ particles are mobile. HO$_2$·/O$_2$· formed by the photocatalysis of TiO$_2$ particles immobilized onto the inner surface of a coil-quartz tube were forced under a continuous flow through a knotted tubing reactor (KTR) and into the aqueous phase completely separated from the TiO$_2$ particles, and were measured by a chemiluminescence (CL) technique using 2-methyl-6-(p-methoxyphenyl)-3,7-dihydroimidazo[1,2-$\alpha$]pyrazin-3-one (MCLA) as the reagent. The initial concentration of the HO$_2$·/O$_2$· stream entering the KTR was determined by its half-life (98 s) at pH 5.8. We suggest that the efficiency of TiO$_2$ photocatalytic reactions may be further improved by utilizing the mobility of HO$_2$·/O$_2$·.

Key Words: TiO$_2$ photocatalyst, Hydroperoxyl/superoxide anion radical, Knotted tubing reactor, Chemiluminescence, MCLA

Introduction

TiO$_2$ photocatalytic reactions have been widely studied in relation to the degradation of environmental pollutants in water and for applications in solar energy conversion and super-hydrophilic materials. To date, most of the work in this area has focused on the photocatalytic activity at the TiO$_2$ interface by studying of the oxidation power of photogenerated hole (h$^+$) and reactive oxygen species such as the hydroxyl radical (·OH), and reactive oxygen species such as the hydroxyl radical (·OH). However, recent studies have paid much more attention to the behaviors of hydroperoxyl/superoxide anion radicals (HO$_2$·/O$_2$·, $a_pK_a$ = 4.80) produced as a result of electron transfer from the TiO$_2$ surface to dissolved oxygen (O$_2$) because an understanding of these behaviors is essential to improve the efficiency of TiO$_2$ photocatalytic reactions by discouraging photoinduced electron-hole (e$^-$-h$^+$) recombination.

Nosaka et al. have recently developed a chemiluminescence (CL) method to detect O$_2$· formation by observing the time dependence of the intensity of luminol dropped on the illuminated alkaline TiO$_2$ suspension. Thereafter, Hirakawa and Nosaka insisted that O$_2$· molecules are adsorbed onto the TiO$_2$ surface and that decay of O$_2$· occurs by the reaction with trapped hole (h$^+$), this result indicates that O$_2$· molecules are not released from the surface of TiO$_2$ particles. Furthermore, Ishibashi et al. reported that most of the photo-generated O$_2$· molecules exist in adsorbed form on the TiO$_2$ surface, and not released during photocatalysis of film-type TiO$_2$, by interpreting the analysis of the O$_2$· decay process, which obeys pseudo-first-order rate kinetics when an excess of luminol and 2-methyl-6-(p-methoxyphenyl)-3,7-dihydroimidazo[1,2-$\alpha$]-pyrazin-3-one (MCLA) is used. In addition, the positive $\zeta$ potentials of TiO$_2$ particles in an aqueous phase during illumination was used to support the adsorptive property of O$_2$· on the surface of illuminated TiO$_2$ particles.

However, almost all of the previous studies reporting this adsorptive property of O$_2$· were limited to being carried out only under strong alkaline (pH > 10) conditions, which is not representative for the photocatalysis of TiO$_2$ that occurs under slight acidic or neutral conditions. Therefore, it remains unclear whether drift HO$_2$·/O$_2$· exist in the photocatalysis of TiO$_2$ particles, and whether they are differentiable from the adsorbed form on the TiO$_2$ surface.

The goal of this study was to examine the mobility of HO$_2$·/O$_2$· molecules generated by the photocatalysis of TiO$_2$ particles; that is, to find whether these molecules can be desorbed and transported into the aqueous phase, which is separated from the adsorbed phase of TiO$_2$ particles. Measurement of the desorbed HO$_2$·/O$_2$· molecules was attempted by passing them under a continuous flow through a knotted tubing reactor (KTR), which was employed to clearly show the migration of these molecules.

Experimental Section

Apparatus and procedures. Figure 1 shows a schematic of the apparatus used for investigating the mobility of HO$_2$·/O$_2$· molecules generated from illuminated TiO$_2$ particles. Pure deionized water was photocatalyzed by illuminated TiO$_2$ particles (size = 325 mesh; anatase 99+%; Sigma-Aldrich) immobilized on the inner surface of a coil-quartz tube (2 mm × 900 mm; inner surface area ≈ 2,826 mm$^2$), which was equipped with a 4-W low-pressure UV Hg lamp ($\lambda_{max}$ = 254 nm; Sankyo Denki Co., Japan). The method for immobilizing the TiO$_2$ particles is reported elsewhere. In addition, the light intensity of a 4-W UV Hg lamp used in this study was analyzed by a chemical actinometer (ferrioxalate) in the coil-quartz tube reactor, and its light intensity was $3.27 \times 10^3$
The HO2/\textsuperscript{•}/O2\textsuperscript{•} stream produced by photocatalysis of the air-saturated TiO\textsubscript{2} surface was forced through a KTR,\textsuperscript{19} which was employed to allow stable migration of the HO\textsuperscript{2/•} molecules with the intention of examining the decay process of their disproportionation in the KTR.\textsuperscript{5} All solutions were delivered by using a peristaltic pump (Ismatec, type ISM 946) with PTFE tubing (i.d. = 0.8 mm; Cole-Parmer, Vernon Hills, IL, USA). Pure deionized water (1.0 mL/min; pH 5.8; Younglin Co., Korea) was used to prevent possible interferences by other anionic compounds, \textit{i.e.}, Cl\textsuperscript{−}, Br\textsuperscript{−}, I\textsuperscript{−}, and SCN\textsuperscript{−}, while measuring HO2/\textsuperscript{•}/O2\textsuperscript{•}.

The HO2/\textsuperscript{•}/O2\textsuperscript{•} stream delivered through the KTR was measured by using MCLA (TCI Co., Japan) as the CL reagent.\textsuperscript{17,20} Because MCLA is not stable at high pH, the reaction between HO2/\textsuperscript{•}/O2\textsuperscript{•} and MCLA was carried out at a pH below 9. MCLA (12 µM) in 1:100 (v/v) ethanol/H\textsubscript{2}O was adjusted to pH 2.5 using HCl,\textsuperscript{20} and was delivered at a flow rate of 1.2 mL/min to join with the HO2/\textsuperscript{•}/O2\textsuperscript{•} stream to generate the CL signal. Desorbed HO2/\textsuperscript{•}/O2\textsuperscript{•} molecules, if any, can be detected as CL as a result of the reaction with MCLA. A spiral quartz cell was designed to mix completely in front of a photomultiplier tube (PMT; Hamamatsu R-374, Shizuoka-ken, Japan). The CL signal was transferred to a data acquisition system, consisting of a signal amplifier, an analog-to-digital (A/D) converter, and a personal computer. In order to identify a reproducible CL signal, all CL measurements are performed in quintuplicate.

**Determination of the HO2/\textsuperscript{•}/O2\textsuperscript{•} concentration desorbed from the surface of illuminated TiO\textsubscript{2} particle.** If HO2 and O2\textsuperscript{•} are desorbed from the photirradiated TiO\textsubscript{2} surface and successfully delivered into the KTR, they will be disproportionated as follows:\textsuperscript{5}

\[
\text{HO}_2^- + \text{HO}_2^- \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \quad (1)
\]

\[
\text{HO}_2^- + \text{O}_2^- + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 + \text{OH}^- \quad (2)
\]

\[
\text{O}_2^- + \text{O}_2^- + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 + 2\text{OH}^- \quad (3)
\]

where \( k_1 = (8.3 \pm 0.7) \times 10^4 \text{ M}^{-1} \text{s}^{-1} \), \( k_2 = (9.76 \pm 0.6) \times 10^7 \text{ M}^{-1} \text{s}^{-1} \), and \( k_3 < 0.3 \text{ M}^{-1} \text{s}^{-1} \). Reaction 3 is believed to be negligible; therefore, the rate of the second-order reaction for HO2/O2\textsuperscript{•} is mainly given by Reactions 1 and 2 is

\[
\frac{d[\text{HO}_2^-/\text{O}_2^-]}{dt} = k_{obs}[\text{HO}_2^-/\text{O}_2^-]_o \quad (I)
\]

where \( k_{obs} = \left(k_1 + k_2(\text{K}_\text{HO}_2^-/\text{[H]}^+)\right)/(1 + K_{\text{HO}_2^-/\text{[H]}^+})^2 \) and \( K_{\text{HO}_2^-/\text{[H]}^+} = 1.6 \times 10^7 \text{ M}^{-1}.\textsuperscript{15} Then, Equation I becomes

\[
\frac{1}{[\text{HO}_2^-/\text{O}_2^-]_o} = k_{obs} \times t + \frac{1}{[\text{HO}_2^-/\text{O}_2^-]_i} \quad (II)
\]

where \([\text{HO}_2^-/\text{O}_2^-]_i\) is the initial concentration of HO2/O2\textsuperscript{•} at the entrance of the KTR (time = zero), and \([\text{HO}_2^-/\text{O}_2^-]_o\) is the concentration of HO2/O2\textsuperscript{•} at time \( t \) after entering the KTR. The initial concentration of HO2/O2\textsuperscript{•} from Equation II can be calculated by Equation III, because \([\text{HO}_2^-/\text{O}_2^-]_i\) is equal to \([\text{HO}_2^-/\text{O}_2^-]_o/2\) at the half-life (\( t_{1/2} \)).

\[
t_{1/2} = \frac{1}{k_{obs} \times [\text{HO}_2^-/\text{O}_2^-]_o} \quad (III)
\]

Therefore, [HO2/O2\textsuperscript{•}]\textsubscript{o} can be readily determined from the \( t_{1/2} \) experimentally and by the value of \( k_{obs} \) at a given pH from the literature.\textsuperscript{5,17,19}

**Results and Discussion**

Figure 2 shows the CL signals corresponding to the concentration of HO2/O2\textsuperscript{•} at a 2 m length in the KTR (retention time: 2 m × 41 s m\textsuperscript{-1} = 82 s) and pH 5.8 when the UV lamp is turned on at 100 s, 750 s, and 1,650 s. The blank test in the absence of MCLA shows no CL signal. The CL signals were measured within a 10% deviation and can be explained as follows. In the aqueous phase, O2 adsorbed on the air-saturated TiO2 surface combines with e\textsuperscript{−} to form O2\textsuperscript{−} or HO2\textsuperscript{•} depending on the pH (pK\textsubscript{HO2−} = 4.80).\textsuperscript{2} Concurrently, various reactive species, such as OH\textsuperscript{−}, h\textsuperscript{+}, e\textsuperscript{−}, and h\textsubscript{tr} (trapped hole),\textsuperscript{1,2,4} can be generated by the photocatalysis of immobilized TiO2 particles. Although these reactive species are present in the coil-quartz tube reactor, they were presumed to be absent in the KTR because of their extremely short life (in the picosecond to millisecond range).\textsuperscript{11} Therefore, HO2/O2\textsuperscript{•} molecules generated by illuminated TiO2 particles can be separated from the various reactive species and passed through the KTR in a continuous flow.

Figure 3 shows the change in the CL intensity with standard deviation versus the length of the KTR (or retention time under a continuous flow). The CL intensity at the y-axis in Figure 3 is a relative value based on the blank CL signal. The CL signals were measured with a 10% deviation and can be explained as follows. In the aqueous phase, O2 adsorbed on the air-saturated TiO2 surface combines with e\textsuperscript{−} to form O2\textsuperscript{−} or HO2\textsuperscript{•} depending on the pH (pK\textsubscript{HO2−} = 4.80).\textsuperscript{2} Concurrently, various reactive species, such as OH\textsuperscript{−}, h\textsuperscript{+}, e\textsuperscript{−}, and h\textsubscript{tr} (trapped hole),\textsuperscript{1,2,4} can be generated by the photocatalysis of immobilized TiO2 particles. Although these reactive species are present in the coil-quartz tube reactor, they were presumed to be absent in the KTR because of their extremely short life (in the picosecond to millisecond range).\textsuperscript{11} Therefore, HO2/O2\textsuperscript{•} molecules generated by illuminated TiO2 particles can be separated from the various reactive species and passed through the KTR in a continuous flow.
Mobility of HO2·/O2·- Generated from TiO2 Photocatalysis

Figure 2. The representative chemiluminescence (CL) signal corresponding to the concentration of HO2·/O2·- (2 m length of knotted tube reactor [KTR], pH 5.8).

Figure 3. Chemiluminescence (CL) intensity versus length of the knotted tube reactor (KTR); pH 5.8, [MCLA] = 12 µM.

Figure 4. Plot of 1/[HO2·/O2·-] against the retention time in the KTR; pH 5.8, [MCLA] = 12 µM.

Figure 5. Schematic of the mobile HO2·/O2·- generated from illuminated TiO2 particles.

the non-ionic characteristics of HO2· tends to diffuse from the TiO2 surface into an available aqueous phase, although their quantity (9%, pKa of HO2·/O2·- = 4.8; Ref. 5) is less at pH 5.8. Furthermore, the TiO2 surface is reportedly more hydrophilic during UV illumination,23 contributing to this desorption.

Conclusions

In this study, HO2·/O2·- generated from the surface of illuminated TiO2 particles were found to be mobile, by using MCLA as the CL reagent. The initial concentration of drift HO2·/O2·- was determined to be 1.07 nM, utilizing the characteristics of disproportionation of HO2·/O2·- and the half-life measured in this study. We suggests that the efficiency of TiO2 photocatalytic reactions may be further improved by utilizing the mobility of HO2·/O2·-.

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