Experimental Evidence of the Mobility of Hydroperoxyl/Superoxide Anion Radicals from the Illuminated TiO₂ Interface into the Aqueous Phase

Bum Gun Kwon and Jeyong Yoon[*]

School of Chemical and Biological Engineering, College of Engineering, Seoul National University, Seoul 151-742, Korea. [*]E-mail: jeyong@snu.ac.kr
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The understanding of behaviors of hydroperoxyl/superoxide anion radicals (HO$_2^\cdot$/O$_2^{\cdot-}$) 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$_2^\cdot$/O$_2^{\cdot-}$ generated on the surface of illuminated TiO$_2$ particles are mobile. HO$_2^\cdot$/O$_2^{\cdot-}$ 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-dihydro-imidazo[1,2-*a*]pyrazin-3-one (MCLA) as the reagent. The initial concentration of the HO$_2^\cdot$/O$_2^{\cdot-}$ stream entering the KTR was determined by its half-life (98 s) at pH 5.8. We suggests that the efficiency of TiO$_2$ photocatalytic reactions may be further improved by utilizing the mobility of HO$_2^\cdot$/O$_2^{\cdot-}$.

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.[1,2] 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).[1-4] However, recent studies have paid much more attention to the behaviors of hydroperoxyl/superoxide anion radicals (HO$_2^\cdot$/O$_2^{\cdot-}$, pK_a = 4.80)[5] produced as a result of electron transfer from the TiO$_2$ surface to dissolved oxygen (O$_2$),[6-12] because an understanding of these behaviors is essential to improve the efficiency of TiO$_2$ photocatalytic reactions by discouraging photoinduced electronhole (e$^-$-h$^+$) recombination.[13-15]

Nosaka *et al.*[6] have recently developed a chemiluminescence (CL) method to detect O$_2^{\cdot-}$ formation by observing the time dependence of the intensity of luminol dropped on the illuminated alkaline TiO$_2$ suspension. Thereafter, Hirakawa and Nosaka[3] insisted that O$_2^{\cdot-}$ molecules are adsorbed onto the TiO$_2$ surface and that decay of O$_2^{\cdot-}$ occurs by the reaction with trapped hole (h$^+$), this result indicates that O$_2^{\cdot-}$ molecules are not released from the surface of TiO$_2$ particles. Furthermore, Ishibashi *et al.*[8] reported that most of the photo-generated O$_2^{\cdot-}$ 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$_2^{\cdot-}$ 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-*a*]-pyrazin-3-one (MCLA) is used. In addition, the positive ζ potentials of TiO$_2$ particles in an aqueous phase during illumination was used to support the adsorptive property of O$_2^{\cdot-}$ on

the surface of illuminated TiO$_2$ particles.[16]

However, almost all of the previous studies reporting this adsorptive property of O$_2^{\cdot-}$ were limited to being carried out only under strong alkaline (pH > 10) conditions,[3,6-10] 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$_2^\cdot$/O$_2^{\cdot-}$ 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$_2^\cdot$/O$_2^{\cdot-}$ 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$_2^\cdot$/O$_2^{\cdot-}$ 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$_2^\cdot$/O$_2^{\cdot-}$ 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 (λ_{max} = 254 nm; Sankyo Denki Co., Japan). The method for immobilizing the TiO$_2$ particles is reported elsewhere.[7,8,17] In addition, the light intensity of a 4-W UV Hg lamp used in this study was analyzed by a chemical actinometer (ferrioxalate)[18] in the coil-quartz tube reactor, and its light intensity was 3.27 × 10^{-5}
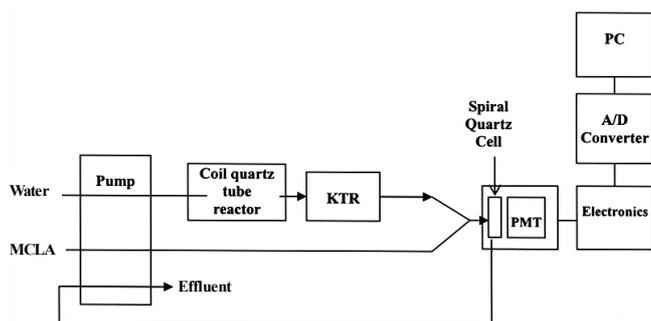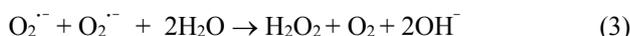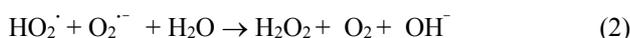
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Figure 1. Schematic of the apparatus for investigating the mobility of $HO_2^./O_2^{.-}$ molecules generated from the surface of illuminated TiO_2 particles. KTR: knotted tube reactor; PMT: photomultiplier tube; A/D converter: analog-to-digital converter.

einstein L^{-1} s^{-1} at 254 nm. The $HO_2^./O_2^{.-}$ stream produced by photocatalysis of the air-saturated TiO_2 surface was forced through a KTR,[19] which was employed to allow stable migration of the $HO_2^./O_2^.$ molecules with the intention of examining the decay process of their disproportionation in the KTR.[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, *i.e.*, Cl^-, Br^-, I^-, and SCN^-, while measuring $HO_2^./O_2^{.-}$.[3]

The $HO_2^./O_2^.$ stream delivered through the KTR was measured by using MCLA (TCI Co., Japan) as the CL reagent.[17,20] Because MCLA is not stable at high pH,[17] the reaction between $HO_2^./O_2^.$ and MCLA was carried out at a pH below 9. MCLA (12 μM) in 1:100 (v/v) ethanol/H_2O was adjusted to pH 2.5 using HCl,[20] and was delivered at a flow rate of 1.2 mL/min to join with the $HO_2^./O_2^{.-}$ stream to generate the CL signal. Desorbed $HO_2^./O_2^.$ molecules, if any, can be detected as CL as a result of the reaction with MCLA. A spiral quartz cell was permitted 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 $HO_2^./O_2^.$ concentration desorbed from the surface of illuminated TiO_2 particle. If $HO_2^.$ and $O_2^{.-}$ are desorbed from the photoirradiated TiO_2 surface and successfully delivered into the KTR, they will be disproportionated as follows:[5]

$$HO_2^. + HO_2^. \rightarrow H_2O_2 + O_2 \quad (1)$$

$$HO_2^. + O_2^{.-} + H_2O \rightarrow H_2O_2 + O_2 + OH^- \quad (2)$$

$$O_2^{.-} + O_2^{.-} + 2H_2O \rightarrow H_2O_2 + O_2 + 2OH^- \quad (3)$$

where $k_1 = (8.3 \pm 0.7) \times 10^5$ M^{-1} s^{-1}, $k_2 = (9.76 \pm 0.6) \times 10^7$ M^{-1} s^{-1}, and $k_3 < 0.3$ M^{-1} s^{-1}. Reaction 3 is believed to be negligible; therefore, the rate of the second-order reaction for $HO_2^./O_2^.$ is

mainly given by Reactions 1 and 2 is

$$-\frac{d[HO_2^./O_2^{.-}]}{dt} = k_{obs}[HO_2^./O_2^{.-}]^2 \quad (I)$$

where $k_{obs} = \{k_1 + k_2 (K_{HO_2}/[H^+])\}/(1 + K_{HO_2}/[H^+])^2$ and $K_{HO_2} = 1.6 \times 10^{-5}$ M^{-1}.[5] Then, Equation I becomes

$$\frac{1}{[HO_2^./O_2^{.-}]_t} = k_{obs} \times t + \frac{1}{[HO_2^./O_2^{.-}]_o} \quad (II)$$

where $[HO_2^./O_2^{.-}]_o$ is the initial concentration of $HO_2^./O_2^{.-}$ at the entrance of the KTR (length = zero), and $[HO_2^./O_2^{.-}]_t$ is the concentration of $HO_2^./O_2^{.-}$ at time t after entering the KTR. The initial concentration of $HO_2^./O_2^{.-}$ from Equation II can be calculated by Equation III, because $[HO_2^./O_2^{.-}]_{t_{1/2}}$ is equal to $[HO_2^./O_2^{.-}]_o/2$ at the half-life ($t_{1/2}$).

$$t_{1/2} = \frac{1}{k_{obs} \times [HO_2^./O_2^{.-}]_o} \quad (III)$$

Therefore, $[HO_2^./O_2^{.-}]_o$ can be readily determined from the $t_{1/2}$ experimentally and by the value of k_{obs} at a given pH from the literature.[5,17,19]

Results and Discussion

Figure 2 shows the CL signals corresponding to the concentration of $HO_2^./O_2^.$ at a 2 m length in the KTR (retention time: 2 m × 41 s m^{-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, O_2 adsorbed on the air-saturated TiO_2 surface combines with e^- to form $O_2^{.-}$ or $HO_2^.$ depending on the pH ($pK_{a, HO_2} = 4.80$).[5] Concurrently, various reactive species, such as $.OH$, h^+, e^-, and h_{tr}^+ (trapped hole),[1,2,4] can be generated by the photocatalysis of immobilized TiO_2 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).[1,2] Therefore, $HO_2^./O_2^.$ molecules generated by illuminated TiO_2 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 intensity decreased as a function of time due to the disproportionation of $HO_2^./O_2^.$ occurring in the KTR, represented by Reactions 1 and 2. The $t_{1/2}$ (or $KTR_{1/2}$) of drift $HO_2^./O_2^.$ in this study was 98 s, as given by the result in Fig. 3 (y = -19.583x + 94; $R^2 = 0.987$). From Equation III and the value for k_{obs} (9.51×10^6 M^{-1} s^{-1}, pH 5.8; Ref. 5) in Equation I, the initial concentration of drift $HO_2^./O_2^.$ was calculated to be 1.07 nM. Using this value of $[HO_2^./O_2^{.-}]_o$, the plot of $1/[HO_2^./O_2^.]$ as a function of the retention time in the KTR is shown in Figure 4. This plot shows an excellent linear relationship indicating the second-order rate kinetics for $HO_2^./O_2^.$. Here,

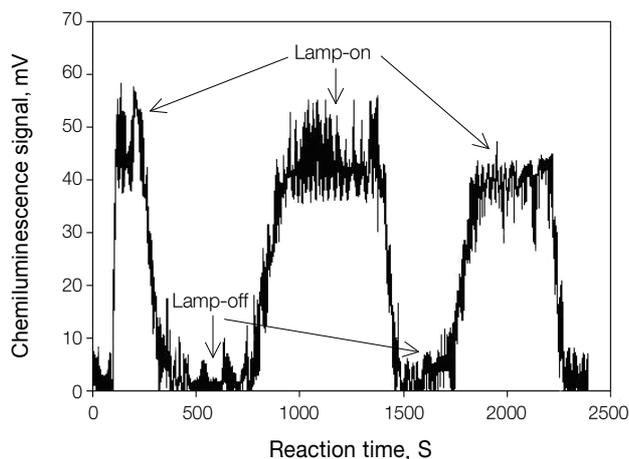**Figure 2.** The representative chemiluminescence (CL) signal corresponding to the concentration of HO$_2$/O$_2^-$ (2 m length of knotted tube reactor [KTR], pH 5.8).
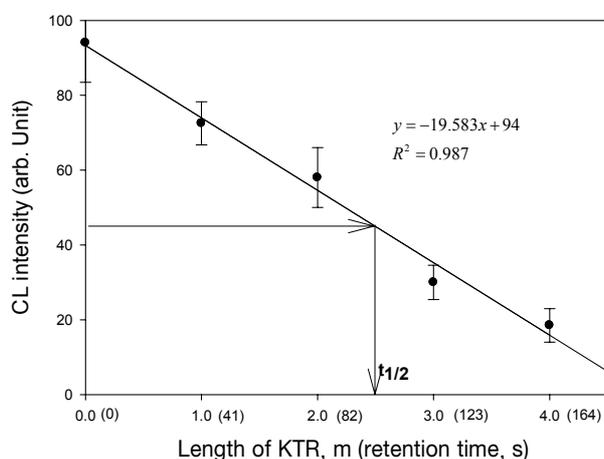

Figure 3. Chemiluminescence (CL) intensity *versus* length of the knotted tube reactor (KTR); pH 5.8, [MCLA] = 12 μM.

the slope of linear regression was found to be about 1.00×10^7, which is acceptable when compared with the value for k_{obs} (9.51×10^6 M^{-1} s^{-1} at pH of 5.8) given by Bielski and Allen.[5]

Positive interference by H$_2$O$_2$ has been reported in a CL method using MCLA as the reagent,[20] and needs to be evaluated in estimating the level of HO$_2$/O$_2^-$ molecules (found in Figure 3) because H$_2$O$_2$ can be formed by the disproportionation (Reactions 1 and 2) of HO$_2$/O$_2^-$.[5] However, as the CL signal generated by the presence of H$_2$O$_2$ is approximately 10,000 times less sensitive than that of HO$_2$/O$_2^-$,[20] this interference is likely to be negligible.[3,6,9,10]

The reaction for the mobility of HO$_2$/O$_2^-$ generated from the surface of illuminated TiO$_2$ particles is illustrated in Figure 5. Briefly, the photocatalysis of TiO$_2$ particles leads to the formation of h$^+$ and e$^-$. ·OH is produced from H$_2$O (or OH$^-$) on the illuminated of TiO$_2$ surface. Subsequently, O$_2$ adsorbed on the air-saturated TiO$_2$ surface act as e$^-$ scavengers and combine with e$^-$ to form HO$_2$/O$_2^-$. Thus, the reduction of O$_2$ by e$^-$ can decrease the recombination of electron-hole (e$^-$-h$^+$) and/or the accumulation of electrons on TiO$_2$ particles. The mobility of HO$_2$/O$_2^-$ can be explained in several ways. First,
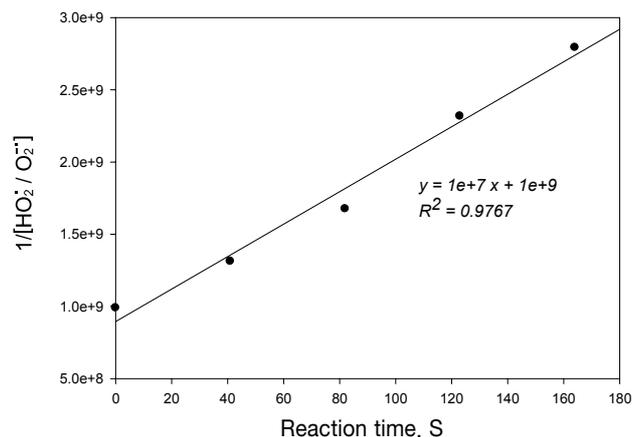

Figure 4. Plot of 1/[HO$_2$/O$_2^-$] against the retention time in the KTR; pH 5.8, [MCLA] = 12 μM.

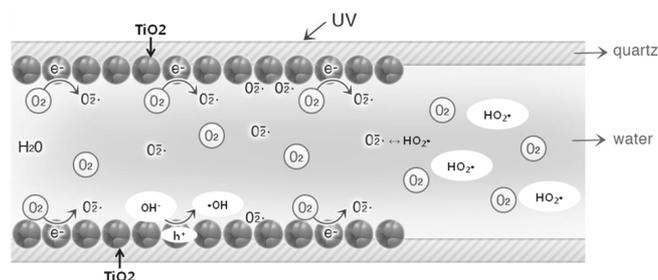**Figure 5.** Schematic of the mobile HO$_2$/O$_2^-$ generated from illuminated TiO$_2$ particles.

the non-ionic characteristics of HO$_2$· tends to diffuse from the TiO$_2$ surface into an available aqueous phase, although their quantity (9%, pKa of HO$_2$/O$_2^-$ = 4.80; Ref. 5) is less at pH 5.8. In addition, the effective Henry's law constant of HO$_2$/O$_2^-$ at pH above 4 increases with pH and contributes to increasing solubility, resulting in more desorption from the TiO$_2$ surface and mobility into the available aqueous phase.[21,22] Furthermore, the TiO$_2$ surface is reportedly more hydrophilic during UV illumination,[23] contributing to this desorption.

Conclusions

In this study, HO$_2$/O$_2^-$ generated from the surface of illuminated TiO$_2$ particles were found to be mobile, by using MCLA as the CL reagent. The initial concentration of drift HO$_2$/O$_2^-$ was determined to be 1.07 nM, utilizing the characteristics of disproportionation of HO$_2$/O$_2^-$ and the half-life measured in this study. We suggests that the efficiency of TiO$_2$ photocatalytic reactions may be further improved by utilizing the mobility of HO$_2$/O$_2^-$.

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