Application of Chemiluminescent Probe to the Characterization of TiO_2 Photocatalysts in Aqueous Suspension

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A chemiluminescent probe, luminol, has been effectively applied to monitor the behavior of superoxide ions ($O_2^{\cdot -}$) at photocatalytic reactions in aerated aqueous suspension of various commercially available TiO_2 powders. By the addition of halide ions, the amount of $O_2^{\cdot -}$ increased or decreased depending on the properties of TiO_2 powders. This difference is discussed with the difference in the mechanism of recombination *via* $O_2^{\cdot -}$ for the photoinduced electron-hole pairs .

Photocatalytic reactions by using semiconductor powder have been paid much interest because of their wide applications such as treatment of waste water.[1] In the photocatalytic reaction of TiO_2 suspension in the air, the primary photocatalytic process may be described as follows:

$$h^+_{VB} + OH^- \rightarrow \cdot OH \tag{1}$$

$$e^-_{CB} + O_2 \rightarrow O_2^{\cdot -} \tag{2}$$

$$O_2^{\cdot -} + h^+_{VB} \rightarrow O_2 \tag{3}$$

$$\cdot OH + \cdot OH \rightarrow H_2O_2 \tag{4}$$

Although the photocatalytic oxidation of reactants proceeds by valence band holes, h^+_{VB}, or $\cdot$ OH radicals, the efficiency is supposed to be limited by the reduction of dissolved O_2 with conduction band electrons, e^-_{CB} (2).[2] In order to study the superoxide radicals, $O_2^{\cdot -}$, we first propose an application of chemiluminescent probing. Merenyi and coworkers investigated the mechanism of chemiluminescence of luminol,[3,4] where $O_2^{\cdot -}$ takes an important role in producing the electronically excited state. The present report shows the difference in the steady-state concentration of $O_2^{\cdot -}$ for various TiO_2 powders under illumination as the effect of halide ions.

Sample was aqueous suspension of 3.5 mL (L = dm^3) containing 0.01M (M = mol dm^{-3}) of NaOH and 15 mg of TiO_2 powder of different sources; P-25 of Japan Aerosil, UV100 of Sachtleben Chemie, and ST-01 of Ishihara Sangyo. These TiO_2 are commonly used as photocatalysts of high activity. The sample was stirred with a magnetic bar in a 1 cm x 1 cm Pyrex cell which was placed in a dark box and irradiated with a 150-W xenon lamp through two glass filters (Hoya U-330 and L39). At the end of the 60-s irradiation, an aqueous solution (50 μL) of 7 mM luminol was injected with a syringe into the sample cell. Chemiluminescence was measured with a photon-counting photomultiplier tube (Hamamatsu Photonics) through a light guide. In front of the entrance of the light guide, another shutter and filter were placed to reduce the prolonged effect of the scattered light. The gate time of photon-counting was 20 ms.

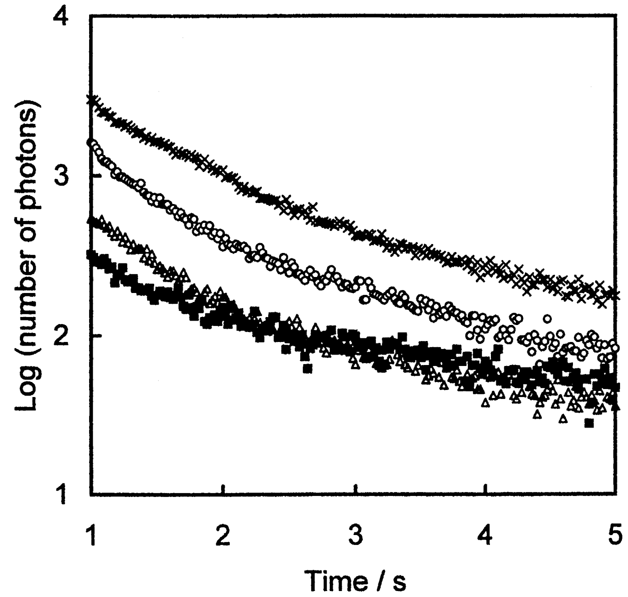

Figure 1. Decay profile of chemiluminescence of luminol. Luminol solution was added after the end of the 60-s irradiation to 3.5 mL aqueous suspension of 15 mg TiO_2 containing 10 mM NaOH; TiO_2 powders are ST-01 (× ○), P-25(△), and UV100(■), and in the presence of 0.1 mM NaCl(×) for ST-01 TiO_2.

Figure 1 is the logarithmic plot of the chemiluminescence intensity as a function of time after the injection of luminol for suspension of various TiO_2 powders. The decay rates at the initial part were nearly the same although the luminescence intensities varied significantly for different TiO_2 powders. The chemiluminescence in the initial part originates from the reaction of luminol with $O_2^{\cdot -}$ and the intensity is proportional to the amount of $O_2^{\cdot -}$. On the basis of separate experiments of adding H_2O_2, chemiluminescence of slower decay was observed and attributed to the reaction of luminol with H_2O_2. Then the observation of slow decay for UV100 TiO_2 indicates that a relatively large amount of H_2O_2 may be produced during the irradiation.

Figure 1 also shows that the chemiluminescence increased for ST-01 TiO_2 in the presence of Cl^- ions while the decay profile was almost unchanged. Chemiluminescence intensity was then measured for

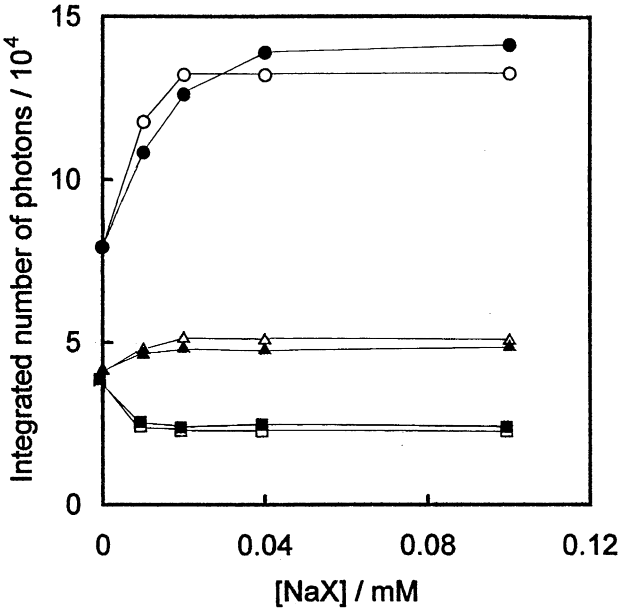

Figure 2. Effect of the amount of sodium halides (NaX) on the integrated chemiluminescence intensities; TiO_2 powders: ST-01(○,●), UV100(△, ▲), and P-25(□,■). Halide ions: I^- (○, △, □) and Cl^- (●,▲,■).

various amounts of halide ions and showed in Figure 2, where the number of photons in 20 ms was integrated over 20 s. With the addition of halide ions, the chemiluminescence intensity increased at first and reached at a steady magnitude for ST-01 and UV100. On the other hand, for P-25 TiO_2 the chemiluminescence intensity was decreased with the initial addition of halide ions. This observation shows that the steady-state concentration of $O_2^{\cdot -}$ was increased or decreased with halide ions, depending on the character of TiO_2 powders. Although halide ions can be oxidized at electrode surface,[5] the first oxidized species would be OH^- at the present small concentration of halide ions. In spite of the one-electron oxidation potentials for I^-, Cl^-, and OH^- in aqueous solution are 1.33,[6] 2.41,[7] and 1.90[8] V *vs.* NHE , respectively, the observed effects of I^- and Cl^- on the chemiluminescence were almost the same. Then, the effect of halide ions may be indirect in the photocatalytic reaction. Since $\cdot$OH radicals react with $O_2^{\cdot -}$ (5) at the rate constant of 1.0×10^{10} $M^{-1}s^{-1}$,[9] this decay process of $O_2^{\cdot -}$ and/or reaction (3) may compete with $O_2^{\cdot -}$ formation (2) in the steady-state.

$$\cdot OH + O_2^{\cdot -} \rightarrow O_2 + OH^- \qquad (5)$$

$$\cdot OH + X^- \rightarrow XOH^- \qquad (6)$$

In the presence of I^- or Cl^- ions, $\cdot$OH radicals may also react with halide ions(6), because the rate constants with $\cdot$OH are 1.2×10^{10} and 4.3×10^9 $M^{-1}s^{-1}$, respectively.[10,11] Thus, the increase in the amount of $O_2^{\cdot -}$ with halide ions observed for ST-01 and UV100 is explained by the decrease in the concentration of $\cdot$OH radicals reacting with $O_2^{\cdot -}$. The opposite observation for P-25 TiO_2 can be understood if reaction (5) is negligible. In an extension of the *in situ* ESR measurement,[12] we found that acetic acid is oxidized directly on P-25 TiO_2 powder, while $\cdot$OH radical mediates the oxidation of acetic acid on UV100 TiO_2, indicating that the amount of $\cdot$OH in the photocatalytic reactions with P-25 TiO_2 is likely too small for reaction (5) to occur. Thus, the decrease in the amount of $O_2^{\cdot -}$ for P-25 could be explained by that halide ions accelerate the surface oxidation of $O_2^{\cdot -}$ (3) during the irradiation. For further discussion the difference in the crystallinity, crystal structure, and particle size of these TiO_2 powders must be taken into consideration. A detailed investigation into the difference in the reaction mechanism of these and other TiO_2 powders is now in progress.

Although only the spin trapping technique[13] of electron spin resonance spectroscopy is used for detecting $O_2^{\cdot -}$ in photocatalytic reactions so far, the present study shows that chemiluminescent probing is also useful to investigate the behavior of $O_2^{\cdot -}$ in the reaction system.

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