Time-resolved Chemiluminescence Study of Photocatalytic Reaction of TiO_2

Xing-Zheng Wu* and Keiko Akiyama
Department of Materials Science and Engineering, Faculty of Engineering, Fukui University, 3-9-1 Bunkyo, Fukui 910-8507

(Received August 19, 2003; CL-030764)

Time-resolved luminol chemiluminescence (CL) with a time resolution of μs in photocatalytic reaction of TiO_2 suspension was reported. It was found that the luminol CL signal was observed after about 15 μs of illumination of a pulse light of 355 nm, and reached maximum at about 40–60 μs, then decreased slowly with time.

Recently, the luminol chemiluminescence (CL) method has been applied to study active oxygen species superoxide anion ($O_2^{\bullet-}$) and hydrogen peroxide (H_2O_2) generated in photoirradiated suspensions of TiO_2[1–3] and TiO_2 films.[4–6] In these experiments, a TiO_2 suspension or film was irradiated with UV light for a certain period of time. Then a shutter was used for stopping the illumination. Luminol solution was added either before or after the illumination, and CL decay was monitored in time scale of second. This method is successful in monitoring and examining behaviors of $O_2^{\bullet-}$ and H_2O_2 in a relative long time scale of second. However, it is difficult to observe initial CL dynamics, for example, in time scale from μs to ms after the UV illumination. Also, it is difficult to obtain information on active oxygen species with short lifetime. On the other hand, time domain for reaction kinetics linked to material transport over the TiO_2 surface is said to be on a time scale from μs to ms.[7] Therefore, time-resolved CL measurement with time resolution of μs will be useful for studying initial reaction mechanism of active oxygen species in TiO_2 photocatalytic system. We have reported a time-resolved CL system with time resolution of ms for photo-initiated CL system.[8] In this work, we report time-resolved CL measurement in TiO_2 suspension with time resolution of μs.

Since TiO_2 can absorb light with wavelength of 350–370 nm, the third harmonic light (355 nm) of a Q-switched Nd:YAG laser (pulse width: 4–6 ns; maximum energy: 4 mJ or 60 mW, frequency: 10 Hz, Continuum, CA, USA) was used as a pulse UV illumination source. The pulse laser was focused to a quartz cell ($1 \times 1 \times 4$ cm) by a lens. Light emission from the cell was collected in perpendicular direction to excitation light by two lenses. A knotch filter was placed between the two lenses for eliminating the 355 nm scattering light. The collected light was directly introduced to a photo multiplier tuber (PMT, Hamamatsu, Japan). A color filter, which permitted light with wavelength larger than 370 nm to pass through, was placed in front of the PMT. Bias voltage of the PMT was −900 V. Signal from the PMT was input into a digital oscilloscope (5 GHz, Sony Tektronics, Japan). Suspension of TiO_2 and luminol solution were prepared by dispersing and dissolving desirable amounts of TiO_2 and luminol in 100 mL of 0.1 mol/L carbonate buffer (pH 10.6), respectively. The TiO_2 suspension and luminol solution were mixed well before illumination of pulse laser. Time-resolved CL experimental results showed that the time resolution of the system was below μs.

Figure 1 shows typical time-resolved CL signals for air-saturated, He and O_2-bubbled luminol/TiO_2 suspension solutions, respectively. It can be seen that CL intensity after 15 μs was greatly decreased for He-bubbled luminol/TiO_2 suspension, while increased for O_2-bubbled one in comparison with the air-saturated one. Therefore, the CL after 15 μs was related with the dissolved oxygen. The higher concentration of the dissolved oxygen was, the higher the time-resolved CL intensity generated.

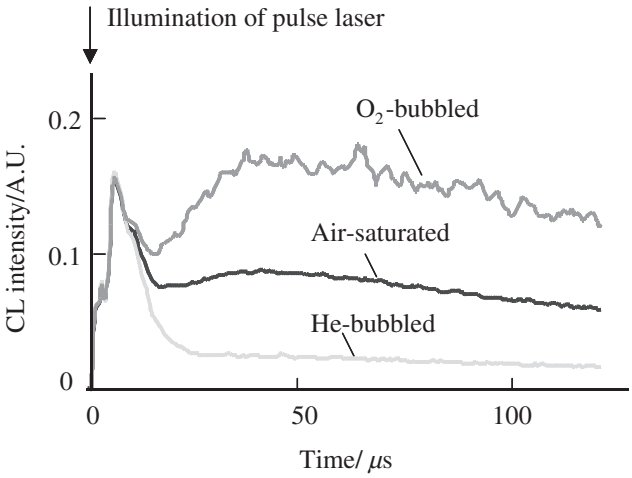

Figure 1. Typical time-resolved CL signals after illumination of pulse laser for air-saturated, He and O_2-bubbled TiO_2 suspensions. Concentration of luminol and TiO_2 were 1.5×10^{-4} mol/L and 0.15 g/L, respectively. Output power of the pulse laser was 0.2 mJ/pulse.

Figure 2 shows the effect of TiO_2 concentration on the time-resolved CL intensity. When concentration of TiO_2 was zero, i.e., solution of luminol, CL intensity increased firstly after illumination of the pulse laser, and reached a maximum at about 5 μs, then decreased. At about 40 μs, CL intensity has decreased to near zero. However, when TiO_2 existed, CL intensity increased again after about 15 μs, and reached another peak at about 40–60 μs. Moreover, the CL intensity after 15 μs increased with TiO_2 concentration. Therefore, the CL after 15 μs was related with some active species generated in the TiO_2 photo-catalyzed reaction. As far as we know, this time-resolved CL with time-resolution of μs in TiO_2 photo-catalyzed reaction has not been reported so far.

From results in Figures 1 and 2, it is concluded that the peak at about 5 μs was not related with TiO_2 photo-catalyzed reaction since no change was observed with increase of either TiO_2 or dissolved oxygen. This luminescence might be related with luminol radical generated by some photochemical reaction during the strong illumination of the pulse laser, and will be discussed elsewhere. On the other hand, the CL after 15 μs was directly generated by active species of the TiO_2 photocatalytic reaction.

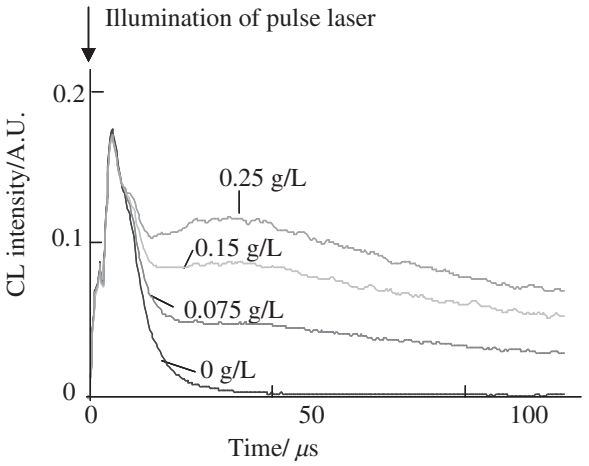

Figure 2. Effect of TiO_2 concentration on time resolved CL signals. Concentration of luminol was 1.5×10^{-4} mol/L. The sample solutions were air-saturated. Output power of the pulse laser was 0.2 mJ/pulse.

In the reported luminol CL in photocatalytic reaction of TiO_2 suspension or TiO_2 film, CL decay caused by $O_2^{\bullet-}$ lasted to several tens seconds[1–6] or even several hundreds seconds[9] after illumination of UV light. Luminol CL caused by H_2O_2 decayed more slowly than the $O_2^{\bullet-}$ generated one.[2] Superoxide dismutase (SOD) and catalase, which are scavengers of $O_2^{\bullet-}$ and H_2O_2, were added into the TiO_2/luminol suspension, respectively. Experimental results showed that the addition of the scavengers gave little decrease in the CL after 15 μs. Furthermore, replacement of luminol by CL reagent MCLA (methoxy cypridina luciferin analogue, 2-methyl-6-(*p*-methhoxyphenyl)-3,7-dihydroimidazo[1,2-a]pyrazin-3-one), which is more selective to detect $O_2^{\bullet-}$[10] and has been used in the reported CL in TiO_2 photocatalytic reaction,[2,6] did not give remarkable CL signal after 15 μs as shown in Figures 1 and 2. Although MCLA molecules may be decomposed in the photocatalytic reaction, it is difficult to consider all MCLA molecules has been completely decomposed during illumination of pulse light. Therefore, the CL signal after 15 μs in this experiment could not be simply explained by the reported $O_2^{\bullet-}$ or H_2O_2-caused luminol CL. It might be related with active oxygen species with short lifetime. The CL signal after 15 μs is also different from photoluminescence of TiO_2[11,12] since no CL was observed when luminol did not exist. The CL spectrum, effect of additions of scavengers of the active oxygen species, and details of the mechanism will be reported later.

The authors thank Dr. H. Inoue of Tokyo Metropolitan University for his helpful discussions. This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (417) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of the Japanese Government.

References

1 Y. Nosaka and H. Fukuyama, *Chem. Lett.*, **1997**, 383.
2 Y. Nosaka, Y. Yamashita, and H. Fukuyama, *J. Phys. Chem. B*, **101**, 5822 (1997).
3 T. Hirakawa, Y. Nakaoka, J. Nishino, and Y. Nosaka, *J. Phys. Chem. B*, **103**, 4399 (1999).
4 K. Ishibashi, Y. Nosaka, K. Hashimoto, and A. Fujishima, *J. Phys. Chem. B*, **102**, 2117 (1998).
5 K. Ishibashi, A. Fujishima, T. Watanabe, and K. Hashimoto, *Electrochemistry*, **69**, 160 (2001).
6 K. Ishibashi, A. Fujishima, T. Watanabe, and K. Hahsimoto, *J. Phys. Chem. B*, **104**, 4934 (2000).
7 A. Yamakata, T. Ishibashi, and H. Onishi, *J. Phys. Chem. B*, **105**, 7258 (2001).
8 X.-Z. Wu, T. Nakayama, K. Uchiyama, and T. Hobo, *Nippon Kagaku Kaishi*, **1997**, 899.
9 T. Hirakawa and Y. Nosaka, *Langmuir*, **18**, 3247 (2002).
10 M. Nakano, M. Sugioka, Y. Ushijima, and T. Goto, *Anal. Biochem.*, **159**, 363 (1986).
11 M. Anpo, M. Tomonari, and M. A. Fox, *J. Phys. Chem.*, **93**, 7300 (1989).
12 M. Anpo, K. Chiba, M. Tomonari, S. Coluccia, M. Che, and M. A. Fox, *Bull. Chem. Soc. Jpn.*, **64**, 543 (1991).

Published on the web (Advance View) November 3, 2003; DOI 10.1246/cl.2003.1108