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Time-Resolved Chemiluminescence of Luminol Induced by TiO_2 Photocatalytic Reactions

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The time-resolved chemiluminescence (CL) of luminol in TiO_2 photocatalytic reactions is reported. Third-harmonic light of 355 nm from a Q-switched Nd:YAG laser was used as a UV light source, and CL was collected in the perpendicular direction to the excitation light by two lenses. After eliminating the scattering light, the CL was detected by a PMT and recorded on a digital oscilloscope. It was found that the CL of luminol induced by the photocatalytic reaction increased with time after the illumination of a pulse laser, and reached the maximum value at about 40–60 µs, then slowly decreased with time. The time-resolved CL intensity increased greatly in an oxygen-bubbled TiO_2 suspension, while it decreased greatly in a He-bubbled one. The total CL intensity increased linearly with the concentration of TiO_2. Scavengers of active oxygen species of $\bullet OH$, $\bullet O_2^-$ and H_2O_2 were added into the suspension for studying the involvement of the active oxygen species. The experimental results suggest that more than about 30% of CL might have been caused by H_2O_2 over the total time period, while the possibility of $\bullet OH$ involvement was small. On the other hand, the addition of a scavenger of $\bullet O_2^-$ had a small effect on the CL in time period of 0–0.7 ms, and decreased the CL after 0.7 ms.

The chemiluminescence (CL) method has been applied to study active oxygen species, such as superoxide anion ($\bullet O_2^-$) and hydrogen peroxide (H_2O_2) generated in photoirradiated suspensions of TiO_2[1–3] and TiO_2 films.[4–6] Luminol and MCLA (methoxy cypridina luciferin analogue), 2-methyl-6-(*p*-methoxyphenyl)-3,7-dihydroimidazo[1,2-*a*]pyrazin-3-one are the most often-used CL reagents because the former reacts with both $\bullet O_2^-$ and H_2O_2, while the later selectively reacts with $\bullet O_2^-$.[7] In these experiments, a TiO_2 suspension or film was irradiated with UV light for a certain period of time. A shutter was then used for stopping the illumination. The luminol solution was added either before or after illumination, and the CL decay was monitored on a time scale of sec. This method was successful for monitoring and examining the behaviors of $\bullet O_2^-$ and H_2O_2 on a relatively long time scale of sec. However, it was difficult to observe the initial CL dynamics, for example, on time scales from µs to ms after UV illumination. Also, it was difficult to obtain information on an active oxygen species with a short lifetime. On the other hand, the time domain for the reaction kinetics linked to material transport over the TiO_2 surface is said to be on a time scale of from µs to ms.[8] Therefore, a time-resolved CL measurement with a time resolution of µs will be useful for studying the initial reaction mechanism of active oxygen species in a TiO_2 photocatalytic system.

We have reported a time-resolved CL system with a time resolution of ms for a photo-initiated CL system.[9] Recently, we further reported on a time-resolved CL system with a time resolution of µs.[10] Furthermore, we demonstrated a unique time-resolved CL of a Luminol/TiO_2 suspension after the illumination of a pulse laser.[10] In this work, we report on the experimental details of time-resolved CL. A preliminary investigation on the involvement of active oxygen species in time-resolved CL was also carried out.

Experimental

Figure 1 shows the experimental setup for the time-resolved CL system. 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 onto a quartz cell (1 cm × 1 cm × 4 cm) by a lens. Light emission from the cell was collected in the perpendicular direction to the excita-

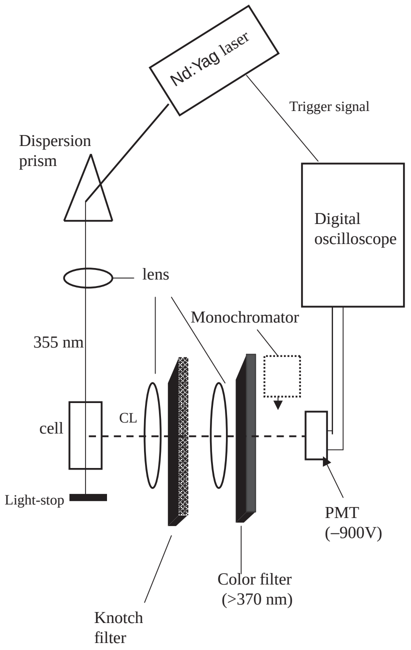

Fig. 1. Experimental setup for the time-resolved CL.

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tion light by two lenses. A knotch filter was placed between the two lenses for eliminating the 355 nm scattered light. The collected light was introduced to a photomultiplier tuber (PMT, Hamamatsu, Japan). A color filter, which permitted light with wavelengths larger than 370 nm to pass through, was placed in front of the PMT. The bias voltage of the PMT was −900 V. The signal from the PMT was input into a digital oscilloscope (5 GHz, Sony Tektronics, Japan). In measuring the CL spectrum, a monochromator was placed between the color filter and the PMT, as shown in Fig. 1.

A suspension of TiO_2 and a luminol solution were prepared by dispersing and dissolving desirable amounts of TiO_2 and luminol in 100 mL of a 0.1 mol/L carbonate buffer (pH 10.6), respectively. A solution of MCLA was prepared by dissolving desirable amounts of MCLA into a phosphate buffer (pH 7.0). The TiO_2 suspension and luminol (or MCLA) solution were mixed well during experiments with a stirring bar in the cell, which was placed above a magnetic stirring plate. The TiO_2 was P25, received from Aerosil Nippon. Superoxide Dismutase (SOD, from bovine erythrocyte, 5250 units/mg), catalase (from bovine liver, 13000 units/mg) and all other reagents were purchased from Wako Chemicals (Japan). Distilled deionized water was used in the experiments.

Results and Discussion

Typical Time-Resolved CL. Figure 2 shows typical time-resolved CL of a luminol solution, a TiO_2–water suspension, and a luminol/TiO_2 suspension from µs to ms after the illumination of a pulse laser under air-saturated conditions. In Fig. 2-A, the large signal soon after the illumination of pulse light is fluorescence from luminol and the scattered light. Then, a peak from 3–15 µs was observed for the luminol solution or luminol/TiO_2 suspensions. The details of this luminescence has not been understood. The difference between the luminol/TiO_2 suspension and TiO_2 suspension or luminol solution was observed after about 15 µs. As shown in Fig. 2-B, the CL intensity decreased near to zero for both the luminol solution and the TiO_2–water suspension at about 30 µs. However, in the luminol/TiO_2 suspension, the CL intensity increased slightly after about 20 µs, reached a maximum at about 40–60 µs, and then slowly decreased. The CL was still detectable in the time range of ms (Fig. 2-C). The CL after 15 µs was also different from the photoluminescence of TiO_2,[11,12] since no CL was observed when luminol did not exist. Therefore, Fig. 2 suggests that the CL of luminol determined after about 15 µs by the present detection system was caused by the photocatalytic reaction of TiO_2.

Effect of Dissolved Oxygen. Figure 3 shows the effect of dissolved gas on the time-resolved CL for the luminol/TiO_2 suspension. It can be seen that CL intensity reached the maximum value at about 3–5 µs for either the He-bubbled or O_2-bubbled or air-saturated luminol/TiO_2 suspension. Because this CL before 15 µs did not change after being bubbled with either He or O_2, it was not related to dissolved oxygen.

On the other hand, the CL intensity after 15 µs was greatly decreased for the He-bubbled luminol/TiO_2 suspension, while it increased for the O_2-bubbled one compared with the air-saturated one. Therefore, the CL after 15 µs was related to the dissolved oxygen. The higher was the concentration of the dissolved oxygen, the stronger was the generated time-resolved CL intensity. On the other hand, bubbling of either He or O_2 had no effect on the time-resolved CL in both the luminol solution and the TiO_2–water suspension. This also suggests that the time-resolved CL after 15 µs was caused by some active oxygen species in the photocatalytic reaction of TiO_2.

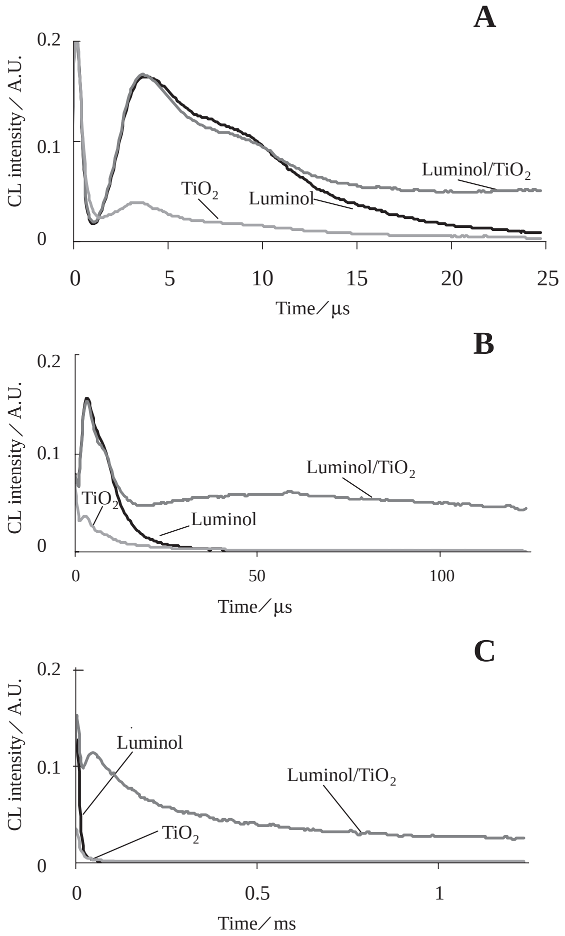

Fig. 2. Typical time-resolved CL signals after the illumination of a pulse laser for the luminol solution, TiO_2 suspension, luminol/TiO_2 suspension. All of the solutions and suspensions were air-saturated. The concentrations of luminol and TiO_2 were 1.5×10^{-4} mol/L and 0.15 g/L, respectively. The output power of the pulse laser was 0.2 mJ/pulse. The time scales for A, B, and C were 0–25 µs, 0–125 µs, and 0–1.25 ms, respectively.

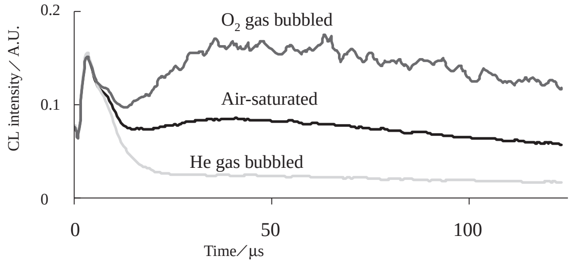

Fig. 3. Effect of dissolved gas on the time-resolved CL of TiO_2 suspensions. Other experimental conditions, except for the bubbling of gases, were the same as those in Fig. 2.

Effect of Concentration of TiO_2. Figure 4-A shows the effect of the TiO_2 concentration on the time-resolved CL

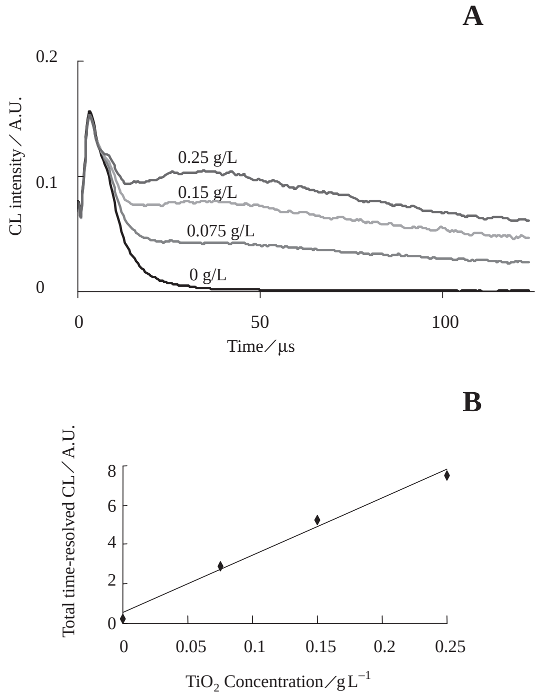

Fig. 4. Effect of the TiO_2 concentration on the time-resolved CL (A) and the relationship between the TiO_2 concentration and the total intensity of time-resolved CL (integration of CL intensity from 20 μs–1.25 ms) (B) for luminol/TiO_2 suspensions. Other experimental conditions were the same as those in Fig. 2.

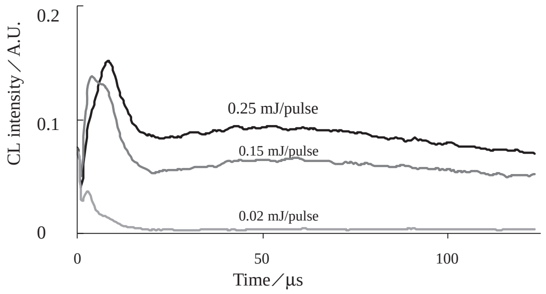

Fig. 5. Effect of the pulse laser power on the time-resolved CL of the luminol/TiO_2 suspension. Other experimental conditions were the same as those in Fig. 2.

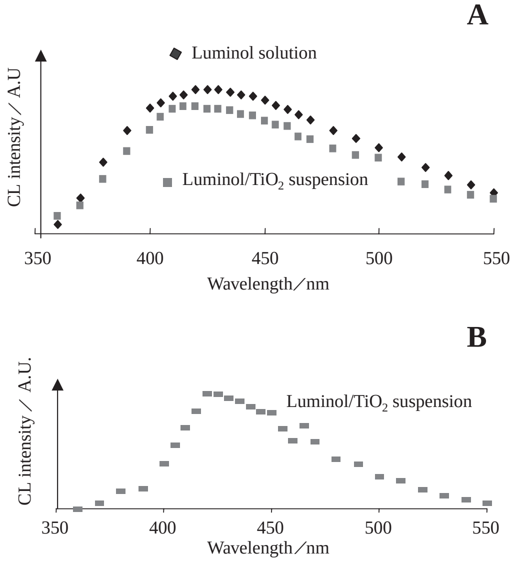

Fig. 6. CL spectrum for the luminol solution and the luminol/TiO_2 suspension. A, measured at 10 μs; B, total CL intensity from 20 μs–1.25 ms. All other experimental conditions were the same as those in Fig. 2.

intensity. It is clear that the time-resolved CL intensity after 15 μs increased with the TiO_2 concentration. This is other stronger evidence that the CL after 15 μs was caused by the TiO_2 photo-catalyzed reaction. Furthermore, the total CL intensity (integration of time-resolved CL from 20 μs to 1.25 ms) was found to have a good linear relation to the TiO_2 concentration (Fig. 4-B). From the viewpoint of application, Figure 4-B means that the total CL intensity could be used for the quantitative determination of the TiO_2 concentration. Also, the luminescence at 3–15 μs did not change with the TiO_2 concentration. This indicated that the phocatalytic reaction did not affect the luminescence at 3–15 μs.

Effect of the Illuminated Light Power. Figure 5 shows the effect of the output power of a pulse laser on the time-resolved CL of luminol/TiO_2 suspensions. It is clear that the larger was the output power of the pulse laser, the larger was the time-resolved CL produced after 15 μs. This might be because that the stronger laser light produced greater amounts of the active oxygen species involved in the CL.

Effect of the Luminol Concentration. The effect of the luminol concentration was also investigated. It was found that both the luminescence at 3–15 μs and CL after 15 μs caused by the TiO_2 photocatalytic reaction changed with the luminol concentration. As stated above, the luminescence at 3–15 μs might have been caused by the luminol radical. The change in the luminol concentration induced a change in the luminol radical concentration, and changed the luminescence intensity at 3–15 μs. Regarding the CL after 15 μs, a decrease of the luminol concentration also decreased the time-resolved CL intensity. This was because the CL after 15 ms was caused by the CL reaction of luminol and the active oxygen species, which might have existed either on the surface of TiO_2 or in the solution. As the amount of luminol increased, the stronger was the CL. Regarding the possibility of CL induced by other active intermediates on the TiO_2 surface instead of the active oxygen species, experimental evidence was not obtained.

CL Spectrum. Figure 6 shows spectra of the CL obtained at 10 μs and the total CL at 20 μs–1.25 ms. In Fig. 6-A, the spectrum for the luminol solution and the luminol/TiO_2 suspension are almost same. The maximum intensity was at about 420 nm. Figure 6-B shows the spectrum of the total CL intensity (integration of time-resolved CL from 20 μs to 1.25 ms). Because the CL intensity became much weaker after passing through a monochromator, the experimental error is relatively large in Fig. 6-B. Figure 6-B also shows that the maximum total CL intensity was at about 420 nm. Although the shape of CL spectra of Figs. 6-A and 6-B was slightly different, they were considered to be typical CL spectrum of luminol in consideration of the experimental error, because the CL spectrum in Fig. 6-A has a similar shape to that in Fig. 6-B for the case that laser power decreased to 0.01 mJ/pulse. A more sensitive measurement of the CL spectrum is necessary to further study the difference between Figs. 6-A and 6-B.

Preliminary Study on Identification of the Involvement of Active Oxygen Species. From results in Figs. 2–5, it is concluded that the luminescence at 3–15 µs was not related to the TiO_2 photo-catalyzed reaction, since no change was observed with an increase of either TiO_2 or dissolved oxygen. Figure 6 shows that the luminescence spectrum at 10 µs was a typical one of luminol CL. This CL might be related to the luminol radical generated by some photochemical reaction during the illumination of a pulse laser. The details remain to be investigated. On the other hand, the CL after 15 µs was directly generated by active oxygen species of the TiO_2 photocatalytic reaction.

In the reported luminol CL for the photocatalytic reaction of the TiO_2 suspension, the CL decay profile after a period of UV illumination showed fast and slow decay components in a time scale of sec. The former decay component was caused by $\bullet O_2^-$, while the latter was by H_2O_2. The CL decay caused by $\bullet O_2^-$ lasted for several tens of seconds,[1–6] or even several hundred seconds.[13] Luminol CL caused by H_2O_2 decayed more slowly than the $\bullet O_2^-$ generated one.[2] In order to investigate whether $\bullet O_2^-$ or H_2O_2 was involved in the time-resolved CL, their scavengers were added into the luminol/TiO_2 suspension.

Figure 7 shows the effect of adding SOD on the time-resolved CL intensity. It is clear that the addition of SOD had little effect on the CL on time scale of 0–70 µs (Fig. 7-A), and increased the CL slightly for a time period of 70 µs–0.7 ms (Fig. 7-B), while it decreased the CL after about 0.7 ms (Figs. 7-B and 7-C). Therefore, it seems that a part of the CL after 0.7 ms was caused by $\bullet O_2^-$, while that before 0.7 ms was not. The reason for this is still not clear. One explanation might be that most of the O_2^- was produced after 0.7 ms, since there were reports that O_2 captured the electron (i.e., the following Eq. 2) at a relatively late time (10–100 µs in gas phase, or even 10–900 µs in water after light illumination).[14,15] It is known that there are many reactions that produce active oxygen species in the TiO_2 photocatalytic system,[16] for example:

$$TiO_2 + \text{UV light} \rightarrow \text{h (hole)} + \text{e (electron)}, \tag{1}$$

$$O_2 + e \rightarrow O_2^-, \tag{2}$$

$$OH^- + h \rightarrow \bullet OH, \tag{3}$$

$$H^+ + O_2^- \rightarrow HO_2, \tag{4}$$

$$HO_2 + e + H^+ \rightarrow H_2O_2, \tag{5}$$

$$2H_2O + 2h \rightarrow H_2O_2 + 2H^+. \tag{6}$$

When SOD existed in the system, the reaction between SOD and O_2^- might have affected the dynamics and increased the production of other active oxygen species, such as H_2O_2 in 0–0.7 ms. Also, the lattice oxygen atom O (L) was reported in the TiO_2 photocatalytic system.[15] This O (L) might also have contributed to the CL in 0–0.7 ms, although there was no further experimental evidence in this experiment.

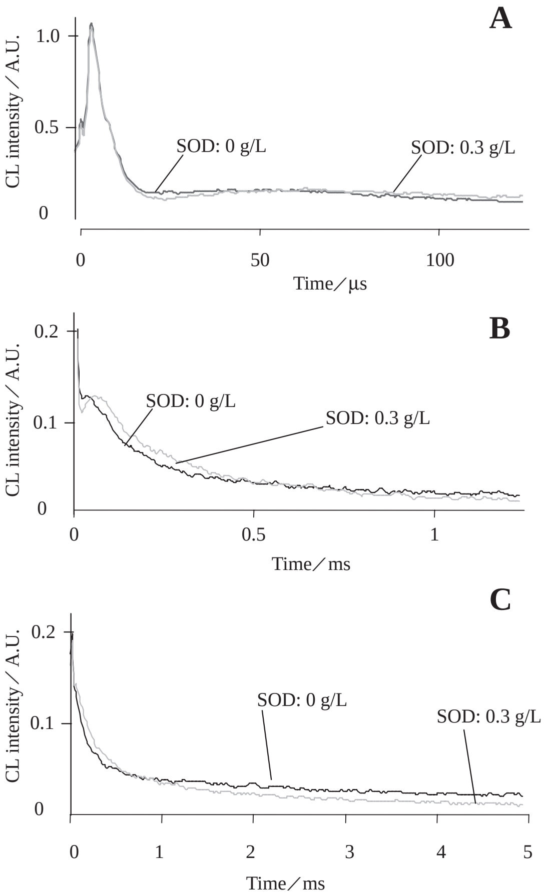

Fig. 7. Effect of SOD on the time-resolved CL of the luminol/TiO_2 suspension. All other experimental conditions were the same as those in Fig. 2.

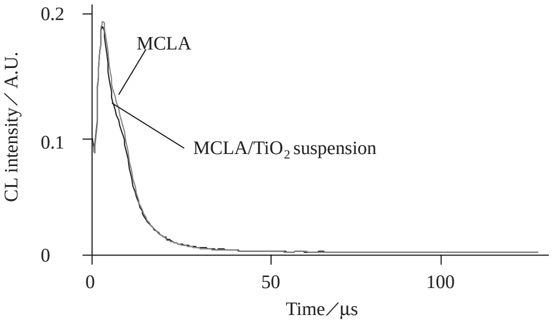

Fig. 8. Time-resolved CL of the MCLA solution and the MCLA/TiO_2 suspension. The concentration of MCLA was 5×10^{-5} mol/L. Both the MCLA solution and the MCLA/TiO_2 suspension were prepared in a pH 7.0 phosphate buffer. All other experimental conditions were the same as those in Fig. 2.

It is known that the CL of MCLA is more selective[7] to the detection of $\bullet O_2^-$, and has been used to identify $\bullet O_2^-$ in the TiO_2 photocatalytic reaction.[2,6] Figure 8 shows a comparison of the time-resolved CL from a MCLA solution and a MCLA–TiO_2 suspension. The time-resolved CL of MCLA solution was the same as that of the MCLA/TiO_2 suspension. The peak at about 10 µs might be caused by the radical of MCLA, caused by the illumination of the pulse laser. Although some MCLA molecules may have been decomposed in the photocatalytic reaction, it is difficult to consider that all of the MCLA molecules were completely decomposed during the illumination of pulse light. In Fig. 8, the CL of MCLA induced by $\bullet O_2^-$ produced in the photocatalytic reaction of TiO_2 had not been detected in the time period of 0–125 µs. The addition of SOD to the MCLA/TiO_2 suspension also decreased time resolved CL after about 0.7 ms. Therefore, a part of the CL after 0.7 ms was caused by $\bullet O_2^-$.

It is well known that the CL method has high sensitivity. Also, $\bullet O_2^-$ is known to be easily produced in the photocatalyitc reaction of air-saturated TiO_2. Therefore, no $\bullet O_2^-$ induced CL in Figs. 7 and 8 suggests that $\bullet O_2^-$ took part in some reactions with a much faster reaction rate than the CL ones in a time period of 0–0.7 ms.

Catalase is known as a scavenger of H_2O_2. Figure 9 shows the effect of catalase on the time-resolved CL of the luminol/TiO_2 suspension. The experimental results showed that the addition of catalase decreased the CL intensity by about 30% in a time period of 0–1.25 ms. Time-resolved CL in time periods of 0–125 µs and 0–5 ms also decreased by about 30% in the presence of catalase. This suggests that at least about 30% of the CL might be caused by H_2O_2 over all time periods.

Mannitol has been used to identify the existence of $\bullet OH$ in the CL of luminol/TiO_2 suspensions, since mannitol is a scavenger of $\bullet OH$.[5] In this work, the effect of mannitol on the time-resolved CL was also investigated. The experimental results showed that the addition of mannitol had little effect on the time-resolved CL. Therefore, the possibility for the involvement of $\bullet OH$ on the time-resolved CL is small.

As a conclusion, luminol CL induced by the TiO_2 photocatalytic reaction increased with time after the illumination of a pulse laser, and reached the maximum value at about 40–60 µs, then decreased slowly with time. The intensities of the time-resolved CL increased greatly in an oxygen-bubbled TiO_2 suspension, while it decreased greatly in a He-bubbled one. The total time-resolved CL intensity increased linearly with the concentration of TiO_2. The experimental results suggest that at least 30% of the CL might be caused by H_2O_2 over all time periods, while the possible involvement of $\bullet OH$ and $\bullet O_2^-$ in the time-resolved CL during 0–0.7 ms was small. This work suggests that the reaction mechanism and reaction dynamics in the initial 1 ms after pulse laser illumination is different from those on a time scale of a second or a min.[2,6] Further details remain to be investigated.

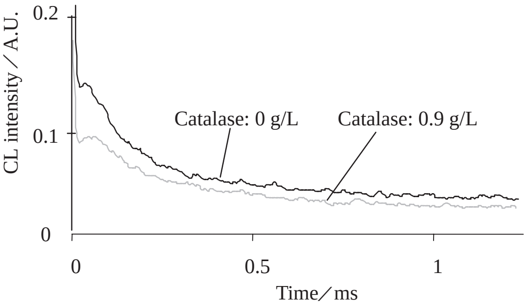

Fig. 9. Effect of catalase on the time-resolved CL of the luminol/TiO_2 suspension. All other experimental conditions were the same as those in Fig. 2.

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