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Time-Dependent Behavior of Active Oxygen Species Formed on Photoirradiated TiO₂ Films in Air

Ken-ichi Ishibashi,[†] Yoshio Nosaka,[‡] Kazuhito Hashimoto,^{*,†,§} and Akira Fujishima^{*,†,||}

Kanagawa Academy of Science and Technology, 1583 Iiyama Atsugi, Kanagawa 243-02, Japan, Department of Chemistry, Nagaoka University of Technology, Kamitomioka, Nagaoka 940-21, Japan, The Research Center for Advanced Science and Technology, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153, Japan, and Department of Applied Chemistry, Faculty of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan

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Active oxygen species formed on TiO₂ film photocatalysts in air were examined by use of a chemiluminescence method. Under relatively strong UV light irradiation, 15 mW cm⁻², two types of active oxygen species formed on the TiO₂ surface were observed after the interception of the excitation light, i.e., one with a shorter lifetime, ca. 3 s, and another with a longer lifetime, ca. 50 s, which may correspond to superoxide (O₂⁻). On the contrary, under relatively weak UV light irradiation, 1 μW cm⁻², only the long-lived species, O₂⁻, was observed. The concentration of O₂⁻ on the TiO₂ surface was saturated even under weak UV illumination, while the short-lived species was not. We suggest that O₂⁻ is deactivated mainly by an electron transfer to surface defects or vacancy sites on the TiO₂ surface. This deactivation reaction proceeds almost independently of coexisting active species.

Introduction

The use of TiO₂ as a photocatalyst for environmental cleanup is of great current interest because of its high photoactivity and chemical stability.¹⁻⁹ We have prepared transparent TiO₂ films with high photocatalytic activity and have demonstrated that these materials show useful self-cleaning, deodorizing, and antibacterial functions even under the weak UV light existing in typical indoor environments.¹⁰⁻¹⁵ As a result, TiO₂ photocatalytic technology is now being applied in the building industry on such interior construction materials as ceramic tiles and window glass.

Despite various efforts, the mechanistic details of the photocatalytic reaction remain unclear. Various mechanisms have been proposed for the photooxidation reactions on the TiO₂ surface. Several types of active oxygen species involved in photocatalytic reactions have been postulated, and some of these have been detected, for example, •OH, which is produced from hydroxyl (OH) groups or adsorbed water on the TiO₂ surface by trapping a hole,¹⁶⁻²⁰ and superoxide, O₂⁻, which forms from an adsorbed oxygen molecule combining with an excited electron. It has also been suggested that further reactions and excitation of O₂⁻ lead to •O, O⁻, and O₃⁻.²¹⁻³²

So far, for the examination of active species produced on TiO₂ surfaces, the electron paramagnetic resonance (EPR) technique has been widely used.³³⁻³⁷ Recently, Nosaka et al. have employed a chemiluminescence technique to the study of photocatalytic reactions in aerated aqueous suspensions of TiO₂ and have demonstrated that this method is useful for monitoring

[†] Kanagawa Academy of Science and Technology.

[‡] Nagaoka University of Technology.

[§] The Research Center for Advanced Science and Technology, The University of Tokyo.

^{||} Department of Applied Chemistry, The University of Tokyo.

the behavior of O_2^- and hydrogen peroxide (H_2O_2) generated in the photocatalytic reaction.^{38,39}

In the present work, we have applied this chemiluminescence method to detect active oxygen species formed on TiO_2 -film-type photocatalysts in air. We have examined the time dependence of active oxygen species remaining on the TiO_2 surface in the dark, which have previously been illuminated with UV light. These observations will provide further information not only on the basic photoactivation processes at semiconductor oxide surfaces but also on the practical application of TiO_2 photocatalysts.

Experimental Section

Soda-lime glass plates coated with silica thin films (ca. 100 nm) were dipped in a titanium isopropoxide solution (Type NDH-520C, Nippon Soda Co. Ltd.). A withdrawal rate of 20 cm min^{-1} was used for all plates. The titanium isopropoxide coating was removed from one side of the plate using ethyl acetate, and the plates were dried in a furnace for 30 min. at 120°C . They were subsequently calcined at 500°C for 1 h in air. The above dip-coating procedure was repeated four times to produce transparent TiO_2 thin films with the anatase crystal structure on one side of the plates. The TiO_2 film thickness was estimated to be ca. $0.4 \mu\text{m}$ on the basis of the interference oscillations in the UV-vis absorption spectra.

Luminol and MCLA (*Cypridina luciferin* analog) were purchased from Wako Pure Chemical Industries and Tokyo Chemical Industry, respectively. The $100 \mu\text{M}$ luminol and MCLA solutions were prepared by dissolving in carbonate buffer ($\text{pH} = 10.01$) and in pure water, respectively.

A $0.9 \text{ cm} \times 0.9 \text{ cm}$ TiO_2 -film-coated glass plate was placed at the bottom of a $1 \text{ cm} \times 1 \text{ cm}$ fused silica standard cell and illuminated with a 200-W high-pressure mercury lamp (Yamashita Denso, HYPERCURE 200) through a UV filter (Toshiba, UV-D36B). UV light illumination was carried out for 10 min. The UV light intensity was controlled using neutral density filters. Aliquots ($200 \mu\text{L}$) of either luminol or MCLA solution were dropped in the dark onto the TiO_2 film, which had previously been illuminated with UV light for 10 min. The chemiluminescence from the TiO_2 surface was observed by use of photon counting. The time at which the UV preillumination was stopped was defined as $t = 0$, and the time interval, t' , from $t = 0$ to the time when the solution was dropped, was controlled from 0 to 60 s. The time dependence of the amounts of active species formed on the TiO_2 were estimated by plotting the integrated chemiluminescence intensity (ICI) in each experimental run as a function of the interval time t' . These procedures are schematically shown in Figure 1.

Results and Discussion

When luminol or MCLA solution was dropped onto the TiO_2 -coated glass that had been preilluminated, broad chemiluminescence in the wavelength regions 370–550 and 400–580 nm, respectively, were observed. The ICI became weaker with increasing time interval t' . No chemiluminescence was, however, detected either when the TiO_2 film had not been illuminated with UV light or when the substrate had not been coated with TiO_2 . These results suggest that the luminescence is caused by chemical reactions of luminol or MCLA with species formed on the TiO_2 via photocatalytic reactions.

It is known that luminol reacts with H_2O_2 emitting strong chemiluminescence in the presence of a metal catalyst.^{40–42} Under our experimental conditions, in which no metal catalyst exists, however, H_2O_2 -induced chemiluminescence is expected

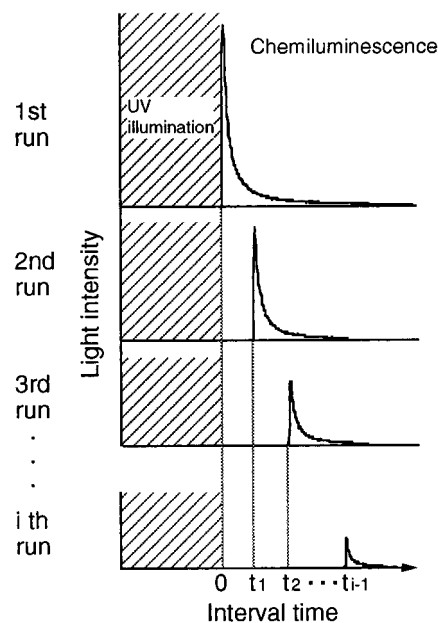


Figure 1. Schematic illustration for the chemiluminescence measurements. Either luminol or MCLA was added at $t' = 0, t_1, t_2, \dots, t_{n-1}$ after stopping the UV illumination. UV light was preilluminated for 10 min before each experimental run.

to be very weak. In fact the addition of luminol to a 30% H_2O_2 solution did not result in detectable chemiluminescence. When $\text{K}_3\text{Fe}(\text{CN})_6$ solution was dropped onto the surface of such a H_2O_2 -luminol solution, the luminescence intensity increased dramatically. However, the luminescence lifetime was ca. 150 s, which is much longer than that observed for the preirradiated TiO_2 surface (a few seconds). Those results show that the luminescence caused by luminol on the preirradiated TiO_2 is not due to H_2O_2 but due to other, more reactive, species. Conversely, it has been established that MCLA reacts specifically with O_2^- and singlet oxygen $^1\text{O}_2$, emitting chemiluminescence.^{43–45} By using the scavengers superoxide dismutase (SOD) and NaN_3 , the active species detected by MCLA in the present experiment was found to be O_2^- . Therefore, a comparison of the time dependency of ICI from luminol and MCLA can provide information on the behavior of photogenerated active oxygen species on TiO_2 in the dark.

In Figure 2 are shown the results obtained with luminol and MCLA with a UV preillumination intensity of 15 mW cm^{-2} . The ICI vs time profiles in parts a and b of Figure 2 indicate the amounts of the active oxygen species reacting with luminol and MCLA, respectively. The decay curve for the former can be approximated by a sum of two exponential functions with lifetimes τ of ca. 3 and ca. 50 s. In contrast, the latter consists of only the $\tau = 50 \text{ s}$ component. Those data suggest that the long-lived component for the decay of luminol corresponds to the deactivation process of O_2^- . Although the identity of the active oxygen species that shows the fast decay for luminol cannot be established, it appears to be more reactive and labile than O_2^- .

Even after decreasing the preillumination UV intensity to $1 \mu\text{W cm}^{-2}$, chemiluminescence was still observed. It should be noted here that this weak UV intensity is almost equivalent to that contained in ordinary room light. Parts a and b of Figure 3 are logarithmic plots of ICI vs t' for luminol and MCLA, respectively. In this case, the fast decay component was not observed even with luminol. However, the lifetime of the slow component was ca. 50 s, which is almost the same as that observed with the strong UV illumination. It is interesting to

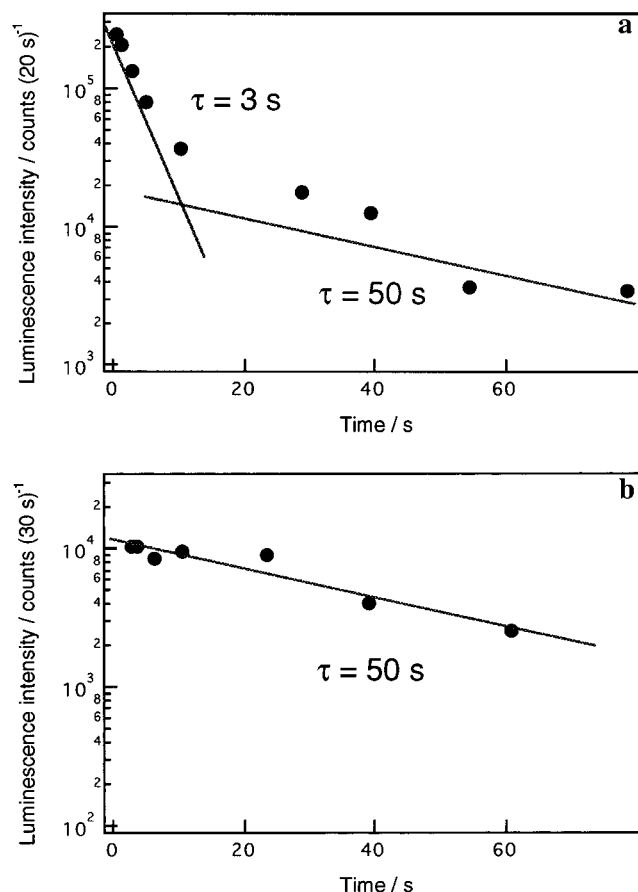
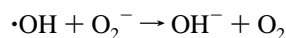


Figure 2. Time dependence of the integrated chemiluminescence intensity after stopping the UV illumination. Preillumination UV intensity was 15 mW cm^{-2} . (a) After contact with luminol solution. (The data were fitted into two straight lines with the indicated time constants.) (b) After contact with MCLA solution. (The data were fitted with a single straight line with the indicated time constant.)

note that the intensity of the slow component from the weakly preilluminated TiO_2 surface is on the same order as that for the strongly preilluminated one, although the UV intensity differed by a factor of greater than 10^4 . This suggests that the concentration of O_2^- on the illuminated TiO_2 surface is nearly saturated under very weak UV illumination. Conversely, the more quickly decaying component, probably a more reactive species such as $\cdot\text{OH}$, $\cdot\text{O}$, or a surface-trapped hole, is not saturated.

Let us consider the deactivation pathways of those reactive intermediates. It is known that $\cdot\text{OH}$ recombines with O_2^- as follows:



Assuming that the main deactivation process is the recombination reaction between O_2^- and the short-lived species, O_2^- should decay at the same rate constant as the short-lived component, at least during the time period that the short-lived species exists on the surface. However, the chemiluminescence decay for MCLA clearly shows that the above assumption is not valid, indicating that the short-lived species and O_2^- decay via different routes. This may be because $\cdot\text{OH}$, $\cdot\text{O}$, and trapped holes are so reactive that they may be deactivated via reaction with organic impurities existing on the TiO_2 surface.

Conversely, the reactivity of O_2^- is relatively low, so that it can be detected up to nearly 1 min on the surface. It is well-known that O_2^- produced in water participates in equilibrium

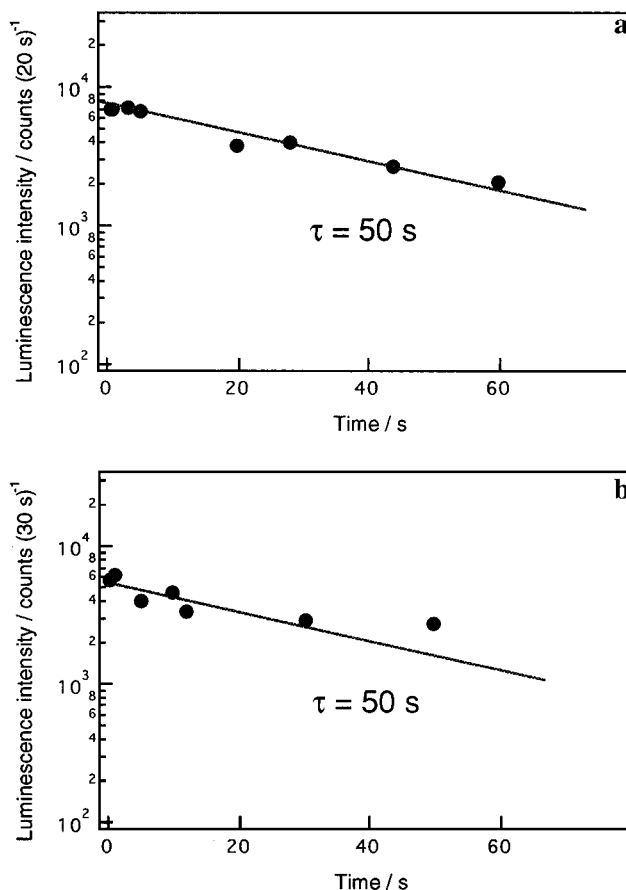
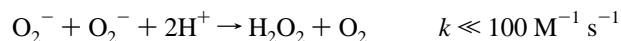
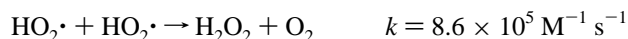
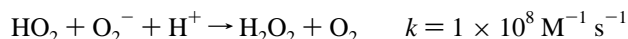


Figure 3. Time dependence of the integrated chemiluminescence intensity after stopping the UV illumination. The preillumination UV intensity was $1 \mu\text{W cm}^{-2}$. The data were fitted with a single straight line with the indicated time constant. (a) After contact with luminol solution. (b) After contact with MCLA solution.

reactions in the presence of protons, as shown below



and is deactivated according to the disproportionation reaction:^{46,47}



Even on the TiO_2 surface in air, similar deactivation pathways could be considered by taking into account the existence of protons from adsorbed water and surface diffusion of adsorbed species. If the above deactivation reactions determine the time dependence of the O_2^- concentration, the decay should obey second-order kinetics. However, the present experiment shows that the O_2^- decay is first-order, suggesting that O_2^- formed on the TiO_2 surface is deactivated by reaction with species present in large excess.

It has been proposed that surface defects such as surface oxygen vacancies are the photocatalytic sites, and, under UV irradiation, O_2 adsorbed at surface defects captures electrons to produce O_2^- .^{30–32} In general, reaction intermediates in the form of adsorbed molecules and atoms may be quite mobile on metal surfaces at reaction temperatures. However, ionic adsorbates on metal oxide surfaces have restricted mobility. Therefore,

the detection of the adsorbates by STM is relatively straightforward, even at a high temperature, e.g., 500 K.^{48–51} A reasonable interpretation of the decay characteristics of O_2^- can be stated in terms of less mobile O_2^- , which does not react with other chemical species existing on the TiO_2 surface, but which is deactivated via release of an electron to TiO_2 , decaying almost independently of other coexisting adsorbed species. In this case, the overall kinetics can be attributed to the recombination of adsorbed O_2^- with the photogenerated holes.

In summary, we have shown that the time-dependent behavior of active oxygen species remaining on the preilluminated TiO_2 surface can be studied by dropping luminol or MCLA solution onto the surface. We were able to distinguish a short-lived reactive species and a long-lived species, the latter probably being O_2^- . The amount of remaining O_2^- was saturated even under weak UV light illumination with a lifetime of ca. 50 s being found. The experimental results also indicate that O_2^- has relatively low mobility and is deactivated by releasing an electron to TiO_2 without reacting with other chemical species.

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