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Author(s)	Hirakawa, Tsutomu; Kominami, Hiroshi; Ohtani, Bunsho; Nosaka, Yoshio
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Mechanism of Photocatalytic Production of Active Oxygens on Highly Crystalline TiO₂ Particles by Means of Chemiluminescent Probing and ESR Spectroscopy

Tsutomu Hirakawa, Hiroshi Kominami,[†] Bunsho Ohtani,[‡] and Yoshio Nosaka*

Department of Chemistry, Nagaoka University of Technology, Kamitomioka, Nagaoka 940-2188, Japan,
Department of Applied Chemistry, Faculty of Science and Engineering, Kinki University, Higashi-Osaka,
Osaka 577-0818, Japan, and Catalysis Research Center, Hokkaido University, Sapporo 060-0811, Japan

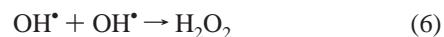
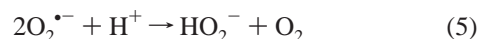
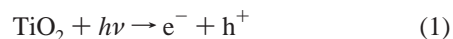
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The effect of calcination on photocatalytic activities was studied for highly crystalline TiO₂ powder, which was synthesized by the method of hydrothermal crystallization in organic media (HyCOM). The productions of O₂^{•−} and H₂O₂ under ambient condition were monitored by means of luminol chemiluminescence probing. The amount of produced O₂^{•−} was decreased with the calcination at lower temperatures in parallel to the decrease of inner Ti³⁺ signal observed at 77 K by ESR spectroscopy. The formation route for H₂O₂ under aerated condition is mainly two-step O₂ reduction in the presence of oxidizable organic molecules such as luminol. Oxidation activity was significantly high when HyCOM-TiO₂ was calcined at higher temperatures, 973–1173 K, as monitored by the amount of oxidized luminol. The observation in ESR measurements and other evidences indicated that the luminol is oxidized via hydroxyl radicals rather than the direct oxidation by photoinduced surface trapped holes.

Introduction

Recently, TiO₂ photocatalysts have been studied with much attention because they can decompose and mineralize pollutant and/or undesirable compounds in air and wastewater.^{1–4} To propagate the practical application, development of highly active photocatalysts is indispensable. One of the strategies of making highly active TiO₂ is to give particles a high crystallinity and a large surface area. The former may reduce the possibility of electron (e[−])–hole (h⁺) recombination at a defective site, while the latter enhance the adsorption of reaction substrates to react with e[−] and h⁺. Kominami and co-workers have synthesized TiO₂ of high crystallinity and large surface area, as well as high thermal stability, by a newly developed method of hydrothermal crystallization in organic media (HyCOM).⁵ The calcined HyCOM-TiO₂ has been reported to show high activities under deaerated conditions in various reactions, such as dehydrogenation of 2-propanol⁶ and deposition of silver metal along with molecular oxygen evolution.⁷ On the other hand, in aerated conditions and in the absence of a sacrificial reagent, mineralization of acetic acid is the only photocatalytic reaction reported with HyCOM-TiO₂.⁸ Therefore, it is of interest to explore the photocatalytic activities of this highly crystallized TiO₂ for the other important reactions under aerated atmosphere.

In the photocatalysis with TiO₂ under aerated conditions, active oxygen species such as superoxide radical (O₂^{•−}), hydroxyl radical (OH[•]), and hydrogen peroxide (H₂O₂) have been noticed as key species to initiate the reactions.⁹ These species are produced photocatalytically as shown by the following equations.



That is, O₂^{•−} and OH[•] are produced by photocatalytic reduction of O₂ (2) and oxidation of H₂O (3), respectively, and then H₂O₂ is produced by the reduction (4) or disproportionation (5) of O₂^{•−}, as well as the dimerization of OH[•] (6). In the (4) and (5), HO₂[−] is changed into H₂O₂ at usual pH since pK_a of H₂O₂ is 11.7.

We have studied the relationship between the properties of TiO₂ powder and the photocatalytic productions of O₂^{•−} and H₂O₂ by means of the luminol chemiluminescent (CL) probe method.^{10,11} The amounts of O₂^{•−} and H₂O₂ produced by TiO₂ photocatalysis were found to correlate well with the secondary particle size and the amount of OH groups in TiO₂ powder.¹¹ Since luminol molecules are also oxidized by the photocatalytic reaction, the formation of active oxygens should be analyzed as the reaction in the presence of the sacrificial electron donor. In some experimental procedures, however, we could monitor them in the absence of the sacrificial reagent as well.¹¹

In the present paper, by using the luminol CL method and ESR spectroscopy, the photocatalytic activity of highly crystallized HyCOM-TiO₂ will be discussed in correlation with the effects of the heat-treatment. In addition, the activity will be

* To whom correspondence should be addressed. E-mail: nosaka@nagaokaut.ac.jp.

[†] Department of Applied Chemistry.

[‡] Catalysis Research Center.

TABLE 1: Properties of TiO₂ Photocatalysts

name	calcination temp/K	anatase component/%	primary particle size ^a /nm	BET surface area ^b /m ² g ⁻¹	secondary particle size/ μ m	amount of OH groups/wt %
HyCOM-non	—	100	17	140	9.7	2.9
HyCOM-573	573	100	18	133	8.9	2.2
HyCOM-823	823	100	23	78	10.7	1.4
HyCOM-973	973	100	39	34	5.1	0.7
HyCOM-1073	1073	73	44	8	7.7	0.3
HyCOM-1173	1173	13	56	3	5.5	0.1
ST-01	—	100	7	320	3.7	5.2
P25	—	80	32	49	1.1	1.8

^a Calculated from line broadening of the anatase (110) peak in XRD pattern. ^b Reference 8.

compared with those of commercially available photocatalytic TiO₂ samples, P25 (Degussa), and ST-01 (Ishihara).

Experimental Section

Materials and Characterization. HyCOM-TiO₂ was synthesized by hydrothermal crystallization in organic media. The details of the synthesis method have been described previously.⁵ The HyCOM-TiO₂ was calcined in an electric furnace at various temperatures under air atmosphere. The rising rate of temperature was as slow as 3 K min⁻¹. After being kept for 1 h at the desired calcination temperatures ranging from 573 to 1173 K, the powder was cooled to the room temperature in the electric furnace. We designate the calcined samples by attaching the calcination temperature such as HyCOM-573. On the other hand, the HyCOM-TiO₂ without calcination was named as HyCOM-non. Commercially available TiO₂ powders, Degussa P25 (Nippon Aerosil, Co. Ltd.) and ST-01 (Ishihara Techno, Co. Ltd.), were generous gifts from the corresponding manufacturers.

The primary particle size and the crystalline composition of the samples were measured by X-ray diffraction (XRD) with a MacScience M03XHF22. BET surface area was measured by a Micromesotechs flowsorbs (Shimadzu 2300) with N₂ gas as an adsorbate. The amount of OH groups of TiO₂ was calculated as the relative decrement of the weight from 423 to 873 K, which was recorded with a TG-DTA meter (Seiko SSC/5200). The secondary particle size of the samples was measured for the suspension in 0.01 M NaOH solutions as the mean Stokes diameter with a centrifugal size distribution meter (Shimadzu SA-CP3). The properties of TiO₂ obtained by the above measurements are listed in Table 1.

For ESR measurements, the TiO₂ sample was placed in an ESR sample tube of 5 mm diameter, and then the tube was degassed at 1×10^{-3} Torr and sealed. The measurements were performed at 77 K with a JEOL ES-RE2X ESR spectrometer under photoirradiation with a 500 W mercury lamp (Ushio, USH 500D) through a band-pass filter (HOYA, U350).

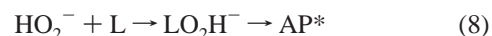
Method of Chemiluminescent Probing. Fifteen milligrams of TiO₂ was suspended in a 1 cm \times 1 cm Pyrex glass cell with 3.5 mL of 0.01 M NaOH aqueous solution of pH 11. The sample cell was mounted on a magnetic stirrer in a dark box. The light source for excitation of TiO₂ was a 150W Xe-lamp (Hamamatsu Photonics, C2499). The excitation wavelength was confined to 387 ± 11 nm or 360 ± 25 nm by using glass filters (HOYA), i.e., a pair of U330 and L39 for 387 nm or U360 for 360 nm. Incident light intensities measured with a photometer (Advantest, TQ8210) were 40 and 3 mW cm⁻², respectively. After the irradiation was switched off with a shutter, luminol CL intensity was monitored with a photon-counting photomultiplier tube (Hamamatsu, R2949). Details for the experimental setup have been described previously.¹⁰

The luminol CL method can be divided into two procedures; post-addition and pre-addition methods. In the post-addition

method, 50 μ L of 7 mM luminol solution was added with a syringe into the TiO₂ suspension immediately after the end of the irradiation. On the other hand, in the pre-addition method, the same amount of luminol solution was added in TiO₂ suspension before the irradiation.

Two schemes for the light irradiation were employed in the experiments. One is single irradiation and another is multiple irradiation. The single irradiation was adopted mainly for the post-addition method, in which the irradiation duration was varied. In the multiple irradiation, the irradiation duration was 10 s and the interval between irradiations was 50 s including 20 s for the CL measurement. This irradiation scheme was adopted mainly in the pre-addition method.

Luminol chemiluminescent reactions observed by these methods involve the following two reactions, (7) and (8), where L^{•-} and L are luminol radical and two-electron-oxidized luminol, respectively.



The reaction product, LO₂H⁻, rapidly decomposes into the excited state of 2-aminophthalate (AP*) which emits the light at around 425 nm. Since the CL intensity is proportional to the formation rate of LO₂H⁻, it is proportional to the concentration products [O₂^{•-}][L^{•-}] and [HO₂⁻][L] for (7) and (8), respectively. Both reactions contribute to the total CL intensity as expressed by the following eq 9, where k_7 and k_8 are the rate constants of the corresponding reactions and Φ is the quantum yield for (8).¹⁰

$$d[\text{AP}^*]/dt = k_7[\text{O}_2^{\bullet-}][\text{L}^{\bullet-}] + \Phi k_8[\text{HO}_2^-][\text{L}] \quad (9)$$

The time profile of CL intensity was analyzed to consist of two decay-components corresponding to the two CL reactions. The fast-decay component, corresponding to the first term in eq 9, is dominant only in the post-addition method where the amount of H₂O₂ is so small that the second term is negligible. The intensity of the fast-decay component which decays exponentially at a rate of about 1 s⁻¹, is proportional to the amount of O₂^{•-} because the amount of L^{•-} is higher than that of O₂^{•-}, although L^{•-} is mainly formed by auto-oxidation. Therefore, from the fast-decay component the amount of O₂^{•-} can be estimated. The slow-decay component with the decay rate of 0.1–0.3 s⁻¹ is dominant in the pre-addition method because a large amount of L is produced by photocatalytic oxidation of luminol. Since L reacts with OH⁻ ions, at pH 11.0 L molecules decompose with the lifetime of 0.25 ms. Thus, the amount of L is represented as a quasi-stationary state. The details of the analysis procedure and kinetic simulation have been described in the previous paper.^{10b}

TABLE 2: Amounts^a of O₂^{•−}, and H₂O₂, and Oxidized Luminol (L) Produced for Various TiO₂ Photocatalysts, HyCOM, ST-01, and P25

sample name	concentration of O ₂ ^{•−} /10 ^{−13} M		concentration of H ₂ O ₂ /μM ^b		concentration of L/10 ^{−19} M ^b
	excitation wavelength = 360 nm	excitation wavelength = 387 nm	luminol present	luminol absent	
HyCOM-no	5.32	0.39	23	13	0.24
HyCOM-573	2.07	0.96	3	12	1.65
HyCOM-823	2.17	0.78	16	8	0.26
HyCOM-973	1.38	0.69	8	7	1.02
HyCOM-1073	1.24	0.78	14	2	1.65
HyCOM-1173	1.50	1.65	38	5	2.76
ST-01	6.47	1.13	19	13	1.52
P25	2.17	0.53	14	9	1.94

^a Steady-state concentration for O₂^{•−} and L and the produced concentration in 10 s for H₂O₂. ^b Excitation wavelength was 387 nm.

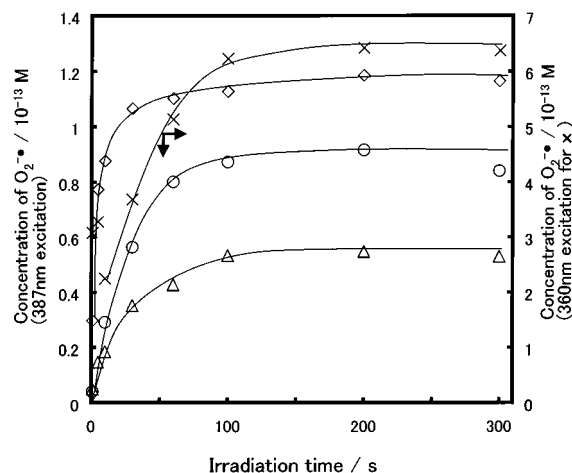


Figure 1. Concentration of O₂^{•−} estimated from chemiluminescence intensity of fast-decay component observed for several kinds of TiO₂ are shown as a function of irradiation time. Excitation wavelength is 387 nm for (◇) ST-01, (△) P25, and (○) HyCOM-823 are plotted on the left ordinate and at 360 nm for (×) ST-01 on the right ordinate.

Experimental Results

Single Irradiation for the Luminol CL Method. Figure 1 shows the amount of O₂^{•−} observed as a function of the duration time of the irradiation in the post-addition method for three kinds of TiO₂; ST-01, P25, and HyCOM-823. The amount of O₂^{•−} increased with irradiation and reached to a steady value at 100 s. Hereafter the irradiation duration of 100 s was employed in the single irradiation experiments. The amounts of O₂^{•−} observed for each TiO₂ by the irradiation at 360 and 387 nm are listed in Table 2. Although the light intensity of 360 nm is lower than that of 387 nm by a factor of 10 or more, the amount of O₂^{•−} with 360 nm excitation was smaller than that with 387 nm excitation. This difference can be explained by the different absorption coefficients at these wavelengths.

Multiple Irradiation for the Luminol CL Method. Figure 2 shows the CL intensity observed after each irradiation on HyCOM-TiO₂ in the pre-addition method where luminol was added in advance. Only the 387 nm light was employed in the multiple irradiation experiment because the light of 360 nm can excite the luminol molecules as well as TiO₂.

The CL intensity of the fast-decay component is relatively small and shows no difference among the TiO₂ photocatalysts as shown in Figure 2. On the other hand, the CL intensity of the slow-decay component, which is governed by the amounts of L and H₂O₂, shows a significant difference. HyCOM-1173 causes a large increase in the CL intensity with the number of irradiation while P25 shows a moderate increase. On the other hands for HyCOM-non, -823, and -973 the CL intensity remains unchanged.

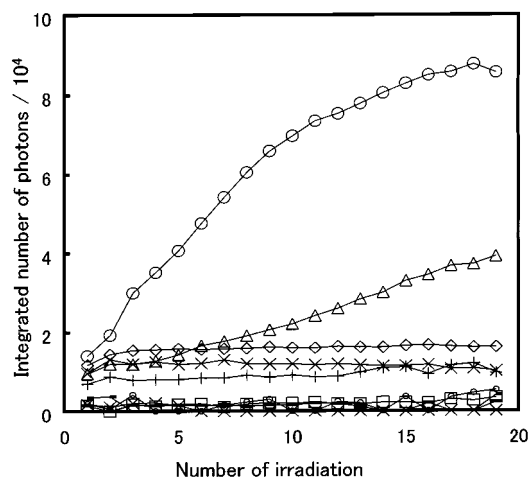


Figure 2. Chemiluminescence intensities for the two decay components observed in the pre-addition experiments. Observed number of photons are integrated over 20 s for each 10 s irradiation and plotted as a function of the number of irradiation. (○, HyCOM-1173; △, P25; ◇, HyCOM-973; ×, HyCOM-823; +, HyCOM-non) Slow-decay component (upper group) and fast-decay component (lower group) correspond to the relative amounts of [H₂O₂]/[L] and [O₂^{•−}], respectively.

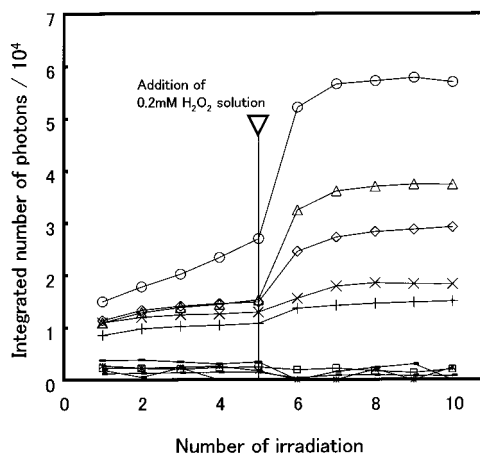


Figure 3. Addition of 0.2 mM H₂O₂ into the sample cell after the end of the 5-th irradiation in the pre-addition experiment of Figure 2. The experimental condition was same as Figure 2. (○, HyCOM-1173; △, P25; ◇, HyCOM-973; ×, HyCOM-823; +, HyCOM-non).

Addition of H₂O₂ in the Multiple Irradiation. Figure 3 shows the effect of the change in the H₂O₂ concentration. When 0.2 mM H₂O₂ was added in the above experiment, the CL intensity of the slow-decay component increased, while that of the fast-decay component remained almost unchanged. The increment of slow-decay component varied for different TiO₂, corresponding to the difference in the amount of produced L

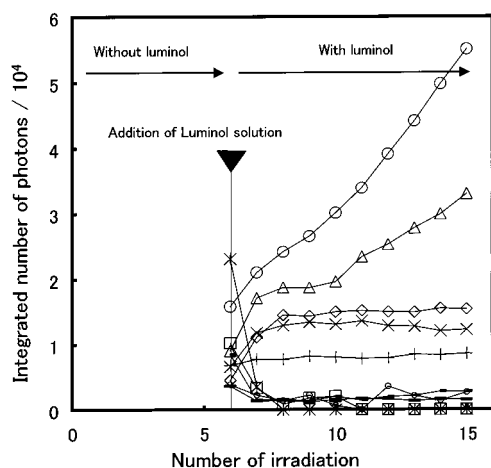


Figure 4. Chemiluminescence intensity of two decay components observed after repeated 10 s irradiations, where luminol was added immediately after the end of the sixth irradiation. (O, HyCOM-1173; Δ , P25; \diamond , HyCOM-973; \times , HyCOM-823; +, HyCOM-non) Slow-decay component (upper group) and fast-decay component (lower group) correspond to the relative amounts of $[\text{H}_2\text{O}_2][\text{L}]$ and $[\text{O}_2^{\cdot-}]$, respectively.

because the amount of added H_2O_2 was larger than that of H_2O_2 produced by TiO_2 photocatalysis. In addition, the amount of produced L is likely constant for each irradiation, as has been proved experimentally in the previous work for P25 TiO_2 .¹¹ Thus, the amount of produced L can be calculated for each TiO_2 with the second term of eq 9 and then listed in Table 2. In this calculation, the CL intensity measured in the initial 20 ms was converted into the value of $d[\text{AP}^{\cdot}]/dt$ with the experimentally determined factor ($1.6 \times 10^{-18} \text{ M s}^{-1}$ for 1 photon/(20 ms)). The following parameters were adopted: $\Phi = 0.012$, $k_8 = 5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, and $[\text{HO}_2^{\cdot}] = 0.03 \text{ mM}$.¹⁰

The amount of H_2O_2 produced by each 10 s irradiation could be calculated by comparing the increment in Figure 3 with the slopes in Figure 2. The concentration of H_2O_2 is listed in Table 2 as the value in the presence of luminol. For HyCOM- TiO_2 , the production of H_2O_2 was increased with the calcination temperature and became higher than that for P25 and ST-01. In this experiment, the intrinsic ability of H_2O_2 formation for each TiO_2 could not be evaluated since luminol is oxidized simultaneously. Then the following experiment was performed.

Addition of Luminol in the Multiple Irradiation. Figure 4 shows the CL intensity of two decay components observed in the multiple irradiation procedure where luminol was added immediately after the sixth irradiation. At the sixth irradiation, the CL intensity of the fast-decay component is large. Since the procedure at the sixth irradiation is the same as that for the single irradiation post-addition method described above, the fast-decay component was significant relative to the slow-decay component. After the seventh irradiation and later, the feature is similar to that in Figure 2. The CL intensity of the slow-decay component observed at the seventh irradiation in Figure 4 is larger than that observed at the first irradiation in Figure 2, indicating that H_2O_2 is produced during six 10-s irradiations in the absence of luminol. Thus, from this difference in the CL intensity, the amount of H_2O_2 produced in the absence of luminol was calculated for one 10-s irradiation and listed in Table 2. This value was smaller than that in the presence of luminol for each TiO_2 and it decreases with increasing the calcination temperature.

ESR Measurements. Figures 5 and 6 represent the ESR spectra measured at 77 K under vacuum for HyCOM- TiO_2

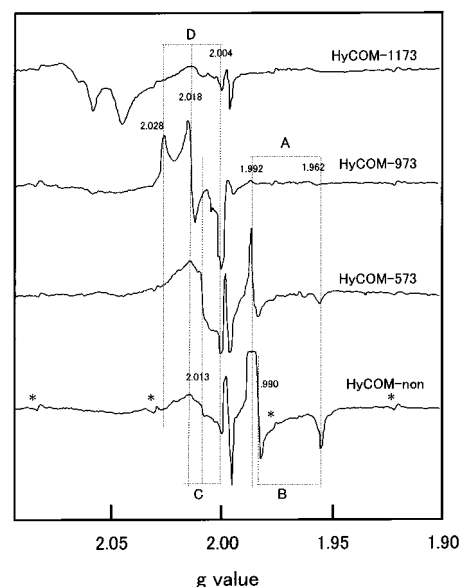


Figure 5. ESR spectra measured at 77 K under irradiation in a vacuum for HyCOM- TiO_2 powders calcined at several temperatures. (*: Mn^{2+} marker).

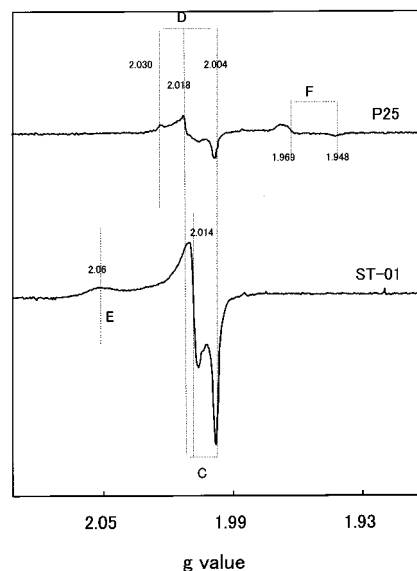


Figure 6. ESR spectra measured at 77 K under irradiation in a vacuum for P25 and ST-01 TiO_2 powders.

calcined at various temperatures and for commercially available TiO_2 , respectively. In Table 3, the assignment of the signals and the relative intensities were listed. The g values obtained for calcined HyCOM- TiO_2 are in good agreement with those reported by Nakaoka and Nosaka for UV100 TiO_2 , where signals B and F were not observed.¹⁴ Signal B was assigned to inner Ti^{3+} since the intensity was not changed with O_2 at 77 K. On the other hand, signal F with $g_1 = 1.948$, $g_2 = g_3 = 1.969$ was assigned to surface Ti^{3+} , which corresponds to the signal with $g_1 = 1.957$, $g_2 = g_3 = 1.990$ for UV100 TiO_2 , since it was decreased in the presence of O_2 and increased with 2-propanol at 77 K. The signal B of HyCOM- TiO_2 was changed into signal A by the calcination, and this signal decreased gradually with increasing the calcination temperature and almost disappeared for HyCOM- TiO_2 calcined at 973 K. In the previous study, the signal A has been also assigned to inner Ti^{3+} radical,¹⁴ and signals C and D have been assigned to the subsurface hole and the surface hole,¹⁴ respectively. The signal D appeared

TABLE 3: The g Values of the ESR Signals Measured at 77 K, Their Assignment,¹⁴ and the Relative Intensities for Each TiO₂ Sample

		signal intensity ^a											
signal	assignment	g			HyCOM						ST-01	P25	
		<i>g</i> ₁	<i>g</i> ₂	<i>g</i> ₃	non	573	823	973	1073	1173			
A	inner Ti ³⁺	1.962	1.992	1.992		40	38	6					
B	inner Ti ³⁺	1.962	1.990	1.990	125								
C	Ti ⁴⁺ –O ^{•−} –Ti ⁴⁺ –OH [−]	2.004	2.014	2.018	6	12					20		
D	Ti ⁴⁺ –O ^{2−} –Ti ⁴⁺ –O ^{•−}	2.004	2.018	2.028			42	18	1			4	
E	O ₂ ^{•−}			2.06							4		
F	surface Ti ³⁺	1.948	1.969	1.969								1	

^a The signal intensity is represented as relative value to that of Mn²⁺ marker at each characteristic g value which is 1.992, 1.990, 2.018, 2.028, 2.06, and 1.969 for signal A, B, C, D, E, and F, respectively.

newly by calcination at 823 K with the decrease of signal C, which is similar observation to the case of UV100 TiO₂.¹⁴

The signals at $g = 2.000$ and $g = 2.048$ – 2.068 were observed for HyCOM-1173 even without UV irradiation. These signals were not observed for calcined UV100 TiO₂ in the previous study.¹⁴ Since the intensity of these signals was not changed with the irradiation, it may be attributable to paramagnetic species which are free from the photoinduced radicals although the assignment has been left to the further study.

As shown in Table 2, TiO₂ powders with a large amount of inner Ti³⁺ at 77 K produced a large amount of O₂^{•−} at ambient temperature, although the inner Ti³⁺ may promote the recombination. The existence of the correlation suggests that the photoinduced e[−]–h⁺ pairs in TiO₂ are stabilized separately at the corresponding trap sites at 77 K and then the e[−] trapped as inner Ti³⁺ could not move to the surface or reaction site at the low temperature. At ambient temperature the inner Ti³⁺ can react with O₂ molecules to produce O₂^{•−}. This explanation is supported by the study of photoluminescence for anatase single crystal, where the behavior of the carriers at trap sites in TiO₂ varies by changing temperature with thresholds at 30 and 150 K.¹⁷

Discussion

O₂^{•−} Formation. In the previous study, we showed that a higher amount of O₂^{•−} is produced photocatalytically with TiO₂ powders of a larger secondary particle size.¹¹ In the present study, the amount of O₂^{•−} produced by 360 nm irradiation did not show a monotonic change with the calcination temperature. Since TiO₂ of the calcined HyCOM did not show significant change in the secondary particle size as shown in Table 1, the present observation does not contradict to the conclusion in our previous report. When the excitation wavelength was 387 nm, the amount of O₂^{•−} increased with increasing the calcination temperature. This increase of O₂^{•−} for HyCOM of higher calcination temperatures above 973 K can be explained by the increase in the number of photons absorbed, since the absorption coefficient of anatase at 387 nm is small than that of rutile crystal. Moreover, although Table 1 shows almost same the physical properties for HyCOM-non and HyCOM-573, a high amount of O₂^{•−} was produced for HyCOM-non relative to HyCOM-573. Therefore, the calcination affects some other properties than those listed in Table 1.

It is probable that HyCOM-non contains an oxidizable organic compound since the titanium butoxide was used in the synthesis by HyCOM method.⁵ To confirm the existence of organic compounds, thermal analysis for HyCOM-TiO₂ was carried out by the thermogravimetry (TG)–differential thermal analysis (DTA) apparatus. Figure 7 represents TG–DTA curves for as-prepared HyCOM-TiO₂. The sharp decrease in the TG curve

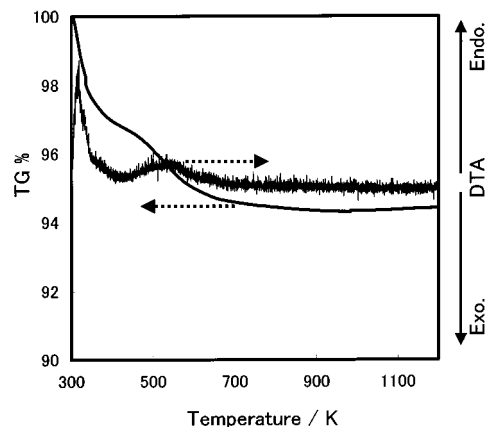


Figure 7. Thermogravimetry (TG) and DTA curve for as-prepared HyCOM TiO₂ (HyCOM-non) powder.

and an endothermic peak in the DTA curve at around 300 K to 430 K is attributable to the desorption of physisorbed water. At a higher temperature, a broad endothermic peak and a rapid weight loss were observed at the temperature around 530 K. This feature was also obtained for HyCOM-573 to a certain extent but not observed for HyCOM-TiO₂ calcined at the higher temperatures. These TG–DTA results suggest that butoxy groups are desorbed on the surface of the HyCOM-TiO₂ at 477–600 K. A similar result has been reported by Kambe et al.¹⁵ They identified the exothermic peak at 493 K in their DSC measurement as *n*-butanol by GC–mass analysis and concluded that the *n*-butoxy groups exist on the surface of untreated HyCOM-TiO₂. In the present study, the number of *n*-butoxy groups on the surface of HyCOM-non was estimated from the weight loss in the TG curve. It was 1757 molecules per one TiO₂ particle of 17 nm diameter, or 5.8 molecules nm^{−2} as the surface density. Thus, the existence of *n*-butoxy groups is responsible for the significant production of O₂^{•−} with HyCOM-non. That is, *n*-butoxy groups trap the photoinduced h⁺ at the surface and then photoinduced e[−] becomes free from the recombination to increase the reduction of O₂.

The amount of O₂^{•−} produced by 360 nm excitation was decreased with the calcination at lower temperatures as summarized in Table 2, while the signal intensity of Ti³⁺ also decreased as shown in Table 3. Then the intensity of inner Ti³⁺ signal is plotted against the amount of O₂^{•−} as shown in Figure 8. The observation of linear correlation in Figure 8 indicates that Ti³⁺ at 77 K is an electron trap site and capable to reduce O₂ to O₂^{•−} at room temperature. By calcination the carrier trap sites are removed and then the ESR signal becomes small.

ST-01 TiO₂ shows the highest activity in O₂^{•−} formation. The ESR spectrum for ST-01 in Figure 6 shows the formation of O₂^{•−} as signal E even at 77 K under vacuum condition, while

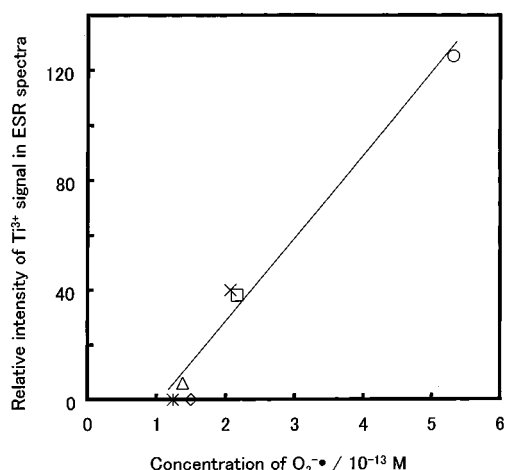
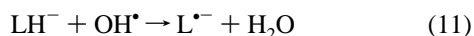


Figure 8. Relative amount of trapped electron Ti^{3+} observed by ESR at 77 K is plotted as a function of the amount of $\text{O}_2^{\bullet-}$ produced in aqueous suspension at room temperature for various HyCOM-TiO₂ calcinated at various temperatures (○, no; ×, 573 K; □, 823 K; △, 973 K; ◇, 1073 K; ◻, 1173 K).

no signal of Ti^{3+} radicals were observed. Therefore, the ST-01 TiO₂ can produce easily the $\text{O}_2^{\bullet-}$ even at 77 K because the primary particle size is so small for inner Ti^{3+} to react with adsorbed O_2 . On the other hand, the P25 TiO₂ shows the signal of surface Ti^{3+} at 77 K and then produces $\text{O}_2^{\bullet-}$ at room temperature. The amount of $\text{O}_2^{\bullet-}$ is comparable to those of HyCOM-TiO₂ calcined at 573–823 K.

Oxidation of Luminol. As shown in Figure 3, the experimental result of H_2O_2 addition with the multiple irradiation allows us to estimate the amount of L produced by the photocatalytic reaction. The photocatalytic oxidation of luminol may take place as follows.



The potential of valence band holes is calculated to be 2.43 eV since the flat band potential of TiO₂ semiconductor at pH 11 is −0.77 V (NHE), based on the reported value of −0.12 V at pH 0.¹² Then irradiated TiO₂ is capable of easily oxidizing LH^- because the redox potential for $\text{L}^{\bullet-}/\text{LH}^-$ is 0.798 V (NHE).¹³ Hydroxyl radical OH which is formed photocatalytically from H_2O (3) can also oxidize LH^- (12) since $\text{OH}^\bullet/\text{OH}^-$ is 1.98 V (NHE). The resulting $\text{L}^{\bullet-}$ produces L, two-electron oxidized form of luminol, by further oxidation (11) or disproportionation (13). As stated above, since the produced L decomposes by OH^- ion in ms, L is observed in a steady state.

The experimental result summarized in Table 2 shows that the amount of L was increased with increasing the calcination temperature. If the amount of L correlates with the BET surface area, the direct oxidation of LH^- ion adsorbed on the TiO₂ surface can be expected. However, the surface area became small for the HyCOM-TiO₂ calcined at a higher temperature. The signal D in the ESR spectra, which is assigned to the surface trapped holes and having ability of direct oxidation, decreased gradually with increasing the calcination temperature. This

observation is not consistent with the assumption that the surface trapped holes oxidized luminol directly. On the other hand, another trapped hole of signal C which has been assigned to the precursor of OH^\bullet radical is observed for ST-01 and HyCOM-573. These TiO₂ produce relatively large amount of L. Since the surface of TiO₂ particles is negatively charged at pH 11, adsorption of LH^- having the same charge would be difficult to occur. Then, the above experimental results suggest that luminol radical $\text{L}^{\bullet-}$ is not formed by the direct oxidation of LH^- (10) but by the indirect oxidation with OH^\bullet radicals (11).

H_2O_2 Formation. For almost all cases, the amounts of H_2O_2 produced in the presence of luminol became large as compared with in the absence of luminol. This experimental result shows that the recombination occurring between $\text{e}^- - \text{h}^+$ pairs or the primary products, $\text{O}_2^{\bullet-}$ and OH^\bullet , were suppressed by the increase of the photocatalytic oxidation of LH^- . In other words, the oxidation of LH^- promotes the photocatalytic reduction of O_2 . Then in the presence of luminol, H_2O_2 is formed mainly from $\text{O}_2^{\bullet-}$. Calcination at the lower temperatures caused a decrease in the amount of H_2O_2 produced with luminol, but it decreased at 1073–1173 K. The former decrease is attributable to the loss of surface butoxy groups and the latter increase is attributable to the increase of $\text{O}_2^{\bullet-}$ at 387 nm irradiation or the increase of oxidation ability represented by the increased amount of L produced. Without organic compounds such as luminol, the amount of H_2O_2 decreased gradually with the calcination temperature. This observation indicated that H_2O_2 is mainly produced from OH radicals which decreased by the reaction with $\text{O}_2^{\bullet-}$.

It seems possible that H_2O_2 is formed by dimerization of OH^\bullet even in the presence of luminol since OH^\bullet is present to oxidize luminol as stated above. To examine the effect of the dimerization of OH^\bullet , chloride ions, which scavenge photoinduced OH radicals, were used in the pre-addition method for P25 and ST-01 TiO₂. If the H_2O_2 is produced by dimerization of OH^\bullet , the amount of H_2O_2 should decrease on the addition of Cl^- ions.¹⁰ The experimental result showed that the CL intensity observed at each irradiation was not decreased with Cl^- ions. Thus, it was confirmed that H_2O_2 was produced mainly from $\text{O}_2^{\bullet-}$ in the presence of sacrificial electron donors.

$\text{O}_2^{\bullet-}$ becomes H_2O_2 in two reaction pathways. One is the photocatalytic reduction (4) and another is the disproportionation of $\text{O}_2^{\bullet-}$ (5). This disproportionation is actually the reaction between $\text{O}_2^{\bullet-}$ and its protonated form, HO_2^\bullet . Since pK_a of HO_2^\bullet is 5.8, disproportionation at pH 11 seems difficult to occur. On the other hand, the photocatalytic reduction of $\text{O}_2^{\bullet-}$ may occur easily. Since the standard redox potential of the reaction 4 is +0.94 V (vs NHE),¹⁶ TiO₂ photocatalyst has enough potential to the reduction of $\text{O}_2^{\bullet-}$ to HO_2^- in aqueous solution even at pH 11. Thus, it is concluded that H_2O_2 is produced from O_2 in air by the two-step reduction.

In the absence of luminol, water is the only oxidizable species. Then H_2O_2 should be produced from OH^\bullet radicals via eqs (3) and (6). The calcination at a higher temperature caused the increase in the oxidation ability represented by the increased amount of L produced, while the amount of H_2O_2 in the absence of luminol was not increased significantly. This observation is consistent with that H_2O_2 is mainly produced from OH radicals which decreased by the reaction with $\text{O}_2^{\bullet-}$. Note that for HyCOM-non the oxidation of butoxy group could be occur and H_2O_2 is produced from the two-step reduction of O_2 .

On the basis of the amount of incident light, we can estimate the photonic efficiency to the production of H_2O_2 . When two photons are absorbed in TiO₂, two H_2O_2 molecules are formally

produces in the absence of luminol and one H_2O_2 molecules are produced in the presence of luminol. By assuming that the light of 40 mW at 387 nm is completely absorbed in TiO_2 suspension of 3.5 mL without reflection, the absorbed photons in the unit of concentration are calculated to be $37 \mu\text{M s}^{-1}$ or $370 \mu\text{M}$ for 10 s. Then the photonic efficiency of H_2O_2 formation for HyCOM-823 in the absence of luminol is calculated to be 2% ($8 \mu\text{M}$) and that for HyCOM-1173 in the presence of luminol to be 21% ($38 \mu\text{M}$). The actual photonic efficiency may be larger than these values because the reflection of anatase in water is about 11%, and the excitation wavelength is so broad that all the light may not be adsorbed.

Conclusion

In the present work, the photocatalytic formations of $\text{O}_2^{\bullet-}$ and H_2O_2 were studied by the luminol CL probe method and ESR spectroscopy for highly crystallized TiO_2 powders produced by HyCOM method. The fact that the amount of $\text{O}_2^{\bullet-}$ produced by photocatalysis of HyCOM- TiO_2 was decreased with increasing the calcination temperature when excitation wavelength was 360 nm. This observation indicates the decrease of trap sites, which was evidenced by the ESR observations at 77 K where Ti^{3+} signal was decreased with the calcination temperature. Although this ESR signal is assigned to inner Ti^{3+} radical, it may not move to the surface or active site due to the stabilization at 77 K but reacts with O_2 adsorbed on the surface at room temperature. Without calcination HyCOM- TiO_2 has peroxy groups on the surface and produces a large amount of $\text{O}_2^{\bullet-}$ by 360 nm excitation, indicating that the peroxy groups react with the photoinduced h^+ to prevent the recombination of $\text{e}^- - \text{h}^+$ pairs.

The capability of H_2O_2 production on HyCOM- TiO_2 was different in the presence and the absence of luminol. In the presence of luminol, the production pathways for H_2O_2 are mainly the two-step reduction of O_2 . On the other hand, in the absence of luminol, dimerization of OH^\bullet may be dominant since the amount of H_2O_2 produced was decreased with the increase of $\text{O}_2^{\bullet-}$. The photonic efficiencies were more than 21% and 2% in the presence and the absence of luminol, respectively.

ESR observations supported the fact that luminol is oxidized preferably by OH^\bullet radicals rather than the direct oxidation of surface h^+ . TiO_2 synthesized by HyCOM method and calcined at 1173 K showed higher activity than commercially available photocatalytic TiO_2 , ST-01 and P25, in the productions of $\text{O}_2^{\bullet-}$

and H_2O_2 and the oxidation of luminol by 387 nm irradiation. On the other hand, ST-01 and P25 TiO_2 showed a higher activity than HyCOM- TiO_2 in the $\text{O}_2^{\bullet-}$ formation by 360 nm irradiation and H_2O_2 formation in the presence of luminol.

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