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Photocatalysis of a transparent titanate aqueous sol prepared from titanium tetraisopropoxide and tetramethylammonium hydroxide

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Abstract

Photocatalysis of a transparent titanate aqueous sol, which was prepared by mixing titanium isopropoxide and tetramethylammonium hydroxide or triethylamine, followed by diluting with water, was examined via the photo-fading of rhodamine B. An irradiation of UV light to the sol containing rhodamine B caused the colour fading by the photocatalytic reactions of the titanate colloids in the sol. The combination of the UV-irradiation with the bubbling of N_2 gas accelerated the fading, whereas that with the bubbling of O_2 led to the decrease in the fading rate, indicating that the fading was caused by the photocatalytic reduction with the titanate colloid, which competed with the photocatalytic reduction of the dissolved oxygen in the sol. On the other hand, the aqueous suspension of a TiO_2 fine powder also exhibited a similar photo-fading of rhodamine B. However, the combination of the photoirradiation with the O_2 bubbling increased the fading rate, whereas that with the N_2 bubbling decreased the fading rate, indicating that the colour fading was caused by the photocatalytic oxidation of rhodamine B with the TiO_2 powder. Consequently, it was found that the photocatalytic reaction mechanism of the titanate sol is different from that of the TiO_2 powder. The cyclic voltammogram of the titanate sols showed that the reduction of rhodamine B adsorbed onto the titanate colloid occurred at a more positive potential than that of rhodamine B itself.

Keywords: Photocatalysis; Photo-fading of rhodamine B; Transparent titanate aqueous sol; Tetramethylammonium hydroxide; Titanium tetraisopropoxide

1. Introduction

TiO_2 films attract increasing attention because of various properties such as ability to photodegrade organic compounds in a wastewater and the amphiphilic [1,2] and superhydrophilic [3] properties. These properties are due to the photocatalytic property of TiO_2. Photocatalyses not only of TiO_2 but also of various materials containing Ti species, such as TiO_2-dispersed silica gels [4–6], zeolites [7–10], and microporous and mesoporous materials with intra-framework Ti atoms [11–17], have been investigated extensively for the purposes to explore a new photocatalyst with a high activity and to add other properties such as a shape-selectivity.

We developed the new preparation method of a titanate sol [18–20]. The sol was prepared by the following procedure; neat titanium isopropoxide ($Ti(OPr^i)_4$) was mixed with a tetraalkylammonium hydroxide or an alkylamine to give a white gel or precipitate, and then the gel or the precipitate was dissolved with water, resulting in a transparent sol. In the cases using alkylamines, a transparent sol could be prepared, only when pK_b of the alkylamine is smaller than 3.3. This indicates that the surface of the titanate colloids is ionised with the amines or OH^- ion via the following reaction; $\equiv TiOH + NH_nR_{3-n} \rightarrow \equiv TiO^- + NH_{n+1}R^+_{3-n}$ or $\equiv TiOH + OH^- \rightarrow \equiv TiO^- + H_2O$. We have already studied the shape and structure of the colloid particles via laser diffraction, TEM, Raman spectra, and XRD measurements [20]. These measurements showed that when the sol with the concentration of 0.5 mol-Ti l^{-1} was prepared by mixing $Ti(OPr^i)_4$ and $(CH_3)_4NOH$ in a ratio of $N/Ti = 0.4–1.0$, the titanate colloids in the sol had the particle size of about 15 nm and the lepidocrocite-type lamellar structure [21–23], $(TMA)_xTi_{2-x/4}Va_{x/4}O_4$, where Va designates a vacancy, with the x value around 0.6. The photocatalyses of titanates with various lamellar structures have been investigated by some workers [24–32]. It has been reported that not only a lamellar titanate itself [24–29] but also a semiconductor-pillared one [28–32] exhibited interesting properties. However, these investigations were conducted by using the powders of the lamellar titanates. As the visual appearance of the titanate sol prepared in this study is transparent, the titanate colloids in the sol might behave like a homogeneous photocatalyst rather than a heterogeneous one. Consequently, it is very interesting to examine the photocatalytic property of the transparent titanate sol.

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The purpose in this study is to examine the photocatalytic property of the transparent titanate sol via the photo-fading of dyes, comparing with that of a representative photocatalyst, a TiO_2 powder.

2. Experimental procedure

2.1. Preparation of the transparent titanate sol

Neat titanium tetraisopropoxide ($Ti(OPr^i)_4$, TIP) was mixed with 15% tetramethylammonium hydroxide (NMe_4OH, TMAOH) aqueous solution, triethylamine (NEt_3), or triethanolamine ($N(C_2H_4OH)_3$, TEOA) in the molar ratio of Ti/N = 1 to give a gel or precipitate, and then the gel or precipitate was dissolved with water, resulting in a transparent sol. The concentration of the sol was adjusted to 0.5 mol-Ti l^{-1}. The photocatalytic ability of the sol was evaluated through the colour fading of rhodamine B or methylene blue added into the sol. The concentrations of rhodamine B and methylene blue were adjusted to 9.0 and 4.5 μM, respectively. For comparisons, the aqueous suspension of the TiO_2 powder (Degussa P-25 with the ratio of anatase/rutile = 3/1) was used. The powder was mixed with water at 0.04 g l^{-1}, which corresponds to 5×10^{-4} mol-Ti l^{-1}. The concentration of the dye was adjusted to the same as that in the titanate sol.

2.2. UV irradiation

The titanate sol or the TiO_2 suspension was poured into a quartz glass test tube with the diameter of 10 mm. A photoirradiation to the sol was conducted under stirring using the light from a super high pressure Hg lamp, which was passed through the optical filter (Toshiba Glass, UV-D33S model) and water. In other words, the UV light of the wavelength range between 230 and 430 nm was irradiated to avoid the photoirradiation to the λ_{max} wavelength of rhodamine B, i.e. 550 nm. Although rhodamine B has the weak absorption around 350 nm, the irradiation to this wavelength could not be avoided.

The photoirradiation under a bubbling of N_2 or O_2 gas was also conducted in order to investigate an influence of concentration of the dissolved O_2 on the photocatalysis. The bubblings of N_2 and O_2 gases may eliminate and increase the dissolved O_2, respectively. These gases were bubbled from the bottom of the test tube using a needle with the inside diameter of 0.5 mm at the flow rate of 50 ml min^{-1}. The bubbling of the gas was carried out for 60 min before the photoirradiation, and then continued during the photoirradiation.

2.3. Evaluation of the photo-fading of the dye

The photo-fading of the dye was evaluated from the change of absorbance at the λ_{max} of the dye in the UV-Vis spectra of the sample solution. In the case of the titanate sol, the photoirradiated sol was transferred into the quartz glass cell (10 mm × 10 mm × 45 mm, Nippon Quartz Glass), and then used for the UV-Vis measurement. In the case of the TiO_2 suspension, the photoirradiated suspension was filtered using a membrane with the pore size of 0.2 μm, and then transferred into the cell. UV-Vis measurement (Hitachi, U-3500 model) was conducted in a transmittance mode using a dual beam. The spectra were recorded in the wavelength range from 800 to 200 nm at the rate of 300 nm min^{-1}.

2.4. Cyclic voltammetry

Cyclic voltammogram was measured in order to observe the redox reactions of rhodamine B in the titanate sol. The concentration of rhodamine B was adjusted to 0.25 mM in order to observe clearly the redox peaks of rhodamine B. The measurements were carried out at an ITO electrode in the potential range between −1.2 and 1.0 V (versus SCE) at the scan rate of 100 mV s^{-1} in an Ar atmosphere. The potential was changed as follows: 0 V (versus SCE) → −1.2 V → 1.0 V → 0 V.

3. Results and discussion

3.1. Photocatalytic reaction of the titanate sol

Fig. 1 shows the change in the UV-Vis spectra of the titanate sol containing rhodamine B by the photoirradiation for the TIP–TMAOH system. The spectra were measured every 2 min. Fig. 2 shows the change of $\ln(C_0/C)$ with photoirradiation period, where C_0 and C designate the concentrations of rhodamine B before and after the photoirradiation, respectively, and were estimated from absorbance at the λ_{max} wavelength of rhodamine B. Figs. 3 and 4 show the change in the UV-Vis spectra by the photoirradiation under a bubbling of N_2 and O_2 gases, respectively. The relations of $\ln(C_0/C)$ with photoirradiation period for these systems are also shown in Fig. 2. In the TIP–TMAOH

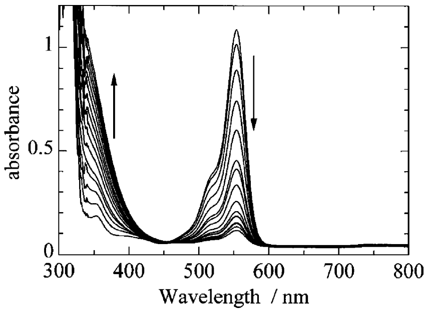


Fig. 1. Photoirradiation–time dependence of the UV-Vis spectra of the titanate sol containing rhodamine B for the TIP–MAOH system. The spectra were measured every 2 min.

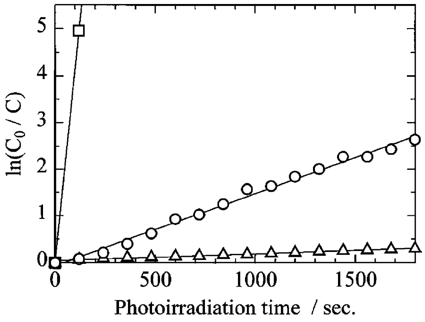


Fig. 2. Time profile of the concentration of rhodamine B in the TIP–TMAOH system and the gas-bubbling dependence of it. The circle, square, and triangle marks represent the results of the systems without the gas bubbling, and with the bubbling of N_2 and O_2, respectively.

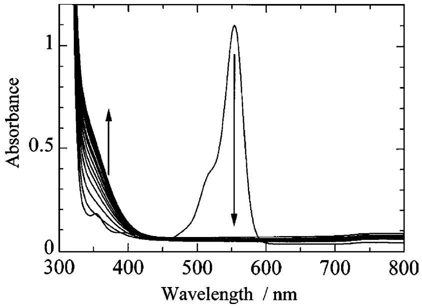


Fig. 3. Change in the UV-Vis spectra of the titanate sol containing rhodamine B by the photoirradiation under the N_2 bubbling for the TIP–TMAOH system. The spectra were measured every 2 min.

system without the gas bubbling, the photoirradiation caused the gradual decrease in absorbance at the λ_{max} of rhodamine B, i.e. at about 550 nm, and a new absorption appeared in the wavelength ranging between 320 to 450 nm. The linear relationship between $\ln(C_0/C)$ and irradiation time was obtained, indicating that the photo-fading was the first-order reaction, whose rate constant was $1.5 \times 10^{-3}\,s^{-1}$. Although also for the aqueous mixture of rhodamine B and TMAOH, the decrease in absorbance at the λ_{max} of rhodamine B was caused by the photoirradiation, the rate constant was as small as $3.4 \times 10^{-5}\,s^{-1}$. These results indicate that the fading of rhodamine B was largely accelerated by the photocatalytic reactions of the titanate species. Next, an influence of the gas bubbling on the colour fading of rhodamine B was examined. The combination of the photoirradiation with the bubbling of N_2 gas drastically accelerated the colour fading of rhodamine B, and the colour of rhodamine B disappeared completely after the photoirradiation for 4 min, whereas the photoirradiation with the O_2 bubbling decreased the fading rate. As the O_2 bubbling increases the concentration of the dissolved oxygen that can be easily reduced, the above results strongly suggest that the fading rate decreased with increase in the concentration of the dissolved oxygen. This indicates that the fading reaction competed with the photocatalytic reduction of the dissolved oxygen, i.e. the photocatalytic reduction of rhodamine B with the titanate colloids in the sol. Fig. 5 shows the UV-Vis spectra of the TIP–TMAOH sols before the photoirradiation, immediately after the photoirradiation under the N_2 bubbling for 30 s, and stirred for 10 min under the air atmosphere after this photoirradiation was stopped. When the titanate sol photoirradiated for as short a period as 30 s was stirred without the irradiation under the air atmosphere, the red colour of rhodamine B reappeared, indicating that the reduced dye was oxidised with the dissolved oxygen. This change strongly suggests that rhodamine B was reduced with the photocatalytic reactions of the sol. Further, in Fig. 5(b), which is the spectrum of the sols immediately after the photoirradiation under the N_2 bubbling for 30 s, a new absorption was observed around 420 nm. Krüeger and Memming [33], Stevens et al. [34], and Langley [35] reported that when rhodamine B was reduced, the absorption of the transient species appeared around 420 nm. Krüeger and Memming [33] and Stevens et al. [34] assigned the transient species to the semi-reduced radical of rhodamine B, i.e. semiquinone. The appearance of the absorption around 420 nm in Fig. 5(b) strongly suggested that rhodamine B was photocatalytically reduced with the titanate sol. However, the sols with a long-period photoirradiation did not exhibit the reappearance of the red colour when the photoirradiation was stopped, and the absorption

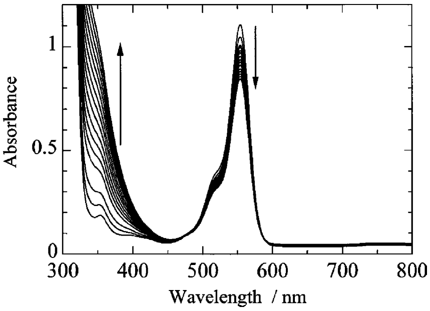


Fig. 4. Change in the UV-Vis spectra of the titanate sol containing rhodamine B by the photoirradiation under the O_2 bubbling for the TIP−TMAOH system. The spectra were measured every 2 min.

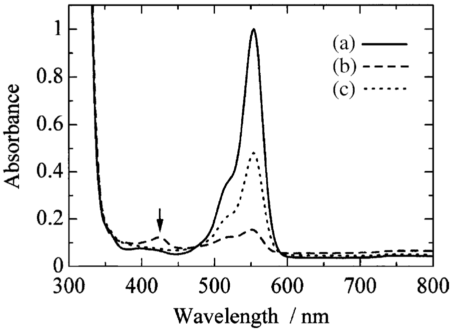


Fig. 5. UV-Vis spectra of the TIP−TMAOH sols: (a) before the photoirradiation, (b) immediately after the photoirradiation under the N_2 bubbling for 30 s, and (c) stirred for 10 min under the air atmosphere after this photoirradiation was stopped. The arrow shows the peak of the transient semi-reduced species of rhodamine B.

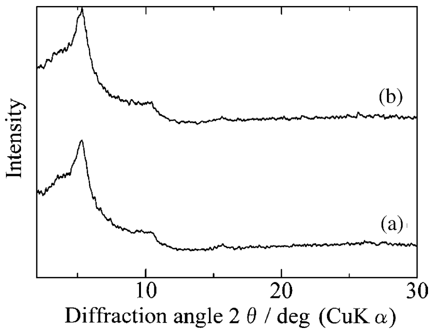


Fig. 6. XRD patterns of the gel films prepared from the titanate sols of the TIP−TMAOH system containing rhodamine B: (a) before, and (b) after the photoirradiation under the N_2 bubbling for 10 min.

around 420 nm. This may show that the longer photoirradiation led to a further photo-reduction of the semireduced rhodamine B.

In order to confirm that the photoinduced reduction of rhodamine B is actually due to the catalytic action of the titanate species, a change in the structure of the titanate colloid by the photoirradiation was examined. The gel films were prepared from the titanate sols of the TIP–TMAOH system containing rhodamine B without and with the photoirradiation with the N_2 bubbling for 10 min. The XRD patterns of these films are shown in Fig. 6. These XRD patterns showed that the interlayer distance of the titanate species was not changed by the photoirradiation, indicating that the structure of the titanate layers was not degraded by the photoirradiation. It is suggested that the photoinduced reaction is the catalytic action of the titanate colloid.

The photoirradiation was also conducted for the TIP–NEt_3 and TIP–TEOA systems, and also caused a similar fading of rhodamine B to the TIP–TMAOH system. The photoirradiation under N_2 bubbling led to the increase in the fading rate, whereas that under O_2 bubbling led to the decrease, suggesting that also in these systems, rhodamine B was photocatalytically reduced with the titanate sols. The rate constants of the colour fading for these systems were summarised in Table 1. The fading rate increased in the following order: TIP−TEOA < TIP–NEt_3 < TIP–TMAOH. This difference in the fading rate is considered later.

For comparisons, the photocatalysis of the TiO_2 fine powder (P-25) was also investigated. As there was a difference in pH values between the titanate sols and the TiO_2 suspension, the photocatalysis of an aqueous suspension containing 5.0×10^{-4} mol l^{-1} of the TiO_2 powder and 0.5 mol l^{-1} of TMAOH, which was the same as the TMAOH concentration in the TIP–TMAOH system, was also investigated. In both the systems of the TiO_2 and TiO_2–TMAOH suspensions, the photo-fading of rhodamine B occurred according to the first-order rate law. The rate constants of the colour fading are summarised in Table 1. Regardless of the addition of TMAOH, the photoirradiation under the N_2 bubbling led to the decrease in the fading rate, whereas that under O_2 bubbling led to the increase. This tendency that the fading rate increased with increase in the concentration of the dissolved oxygen, was opposite to that of the titanate sol, indicating that the fading was the counter reaction to the photocatalytic reduction of the dissolved oxygen, i.e. the photocatalytic oxidation of rhodamine B with the TiO_2 powder. Consequently, the photocatalytic reactions of the TiO_2 powder were different from those the titanate sol.

In order to examine the difference in the photocatalytic reactions between the titanate colloid and the TiO_2 fine powder, cyclic voltammogram was measured for the titanate sols of the TIP–TMAOH and TIP–NEt_3 systems with and without rhodamine B, and for the aqueous mixture of rhodamine B and TMAOH. As NEt_3 is immiscible with H_2O, the measurement could not be carried out for the aqueous mixture of rhodamine B and NEt_3, although NEt_3 is dissolved into the titanate sol via the acid–base reaction with the titanate colloid, as mentioned previously. The negative potential range in their voltammograms is shown in Fig. 7. The titanate sol without rhodamine B exhibited no peaks in the negative potential range. The aqueous mixture of rhodamine B and TMAOH exhibited the peak of a cathodic current at about −1.06 V (versus SCE) during the descent of a potential, and the peak of an anodic current at about −1.00 V during the ascent of a potential, which are assignable to the reduction of rhodamine B and the oxidation of the reduced rhodamine B, respectively. The titanate sols of the TIP–TMAOH and TIP–NEt_3 systems exhibited two reduction peaks around −0.95 and at about −1.1 V during the descent of a potential, and the oxidation peak at −1.0 V during the ascent of a potential. These results show that the existence of the titanate colloid contributes to the appearance of the reduction peak around −0.95 V, which may be assigned to the reduction of rhodamine B adsorbed onto the titanate colloid. As the adsorbed rhodamine B is

Table 1
Rate constants of the fading reaction of rhodamine B on the assumption of the first-order reaction

	TIP–TMAOH	TIP–NEt_3	TIP–TEOA	TiO_2 (P-25)	TiO_2–TMAOH
No bubbling	1.5×10^{-3}	8.9×10^{-4}	5.1×10^{-4}	1.7×10^{-3}	2.7×10^{-3}
N_2 bubbling	4.1×10^{-2}	2.8×10^{-2}	6.7×10^{-4}	1.7×10^{-4}	3.2×10^{-4}
O_2 bubbling	1.5×10^{-4}	3.9×10^{-5}	2.7×10^{-4}	2.2×10^{-3}	6.0×10^{-3}
No bubbling without TIP	3.4×10^{-5}	1.2×10^{-5}	4.1×10^{-6}	5.5×10^{-6}	3.4×10^{-5}
N_2 bubbling without TIP	1.6×10^{-4}	3.5×10^{-5}	8.7×10^{-5}	1.8×10^{-5}	1.6×10^{-4}
O_2 bubbling without TIP	3.4×10^{-5}	1.1×10^{-5}	1.4×10^{-5}	5.5×10^{-6}	3.4×10^{-5}

Unit: s^{-1}.

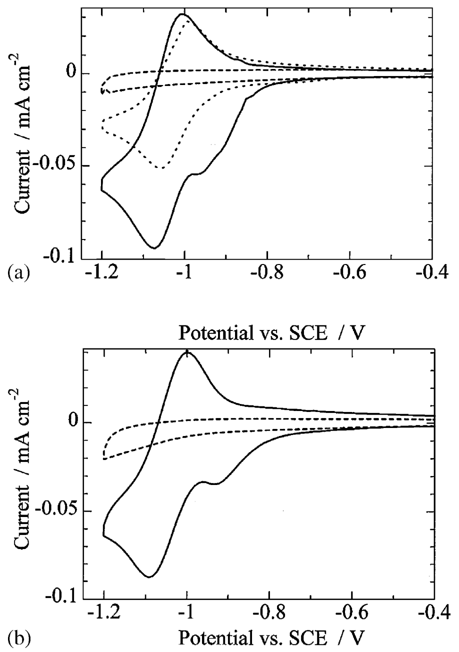


Fig. 7. Cyclic voltammograms of the titanate sols with rhodamine B (solid line) and without rhodamine B (broken line), and the mixture of rhodamine B and TMAOH (dashed line) for the: (a) TIP–TMAOH, and (b) TIP–NEt_3 systems.

reduced at a more positive potential than rhodamine B itself, the titanate sol may lead to the photocatalytic reduction of rhodamine B rather than a photocatalytic oxidation.

3.2. Influence of the basicity of the titanate sol on the fading rate of rhodamine B

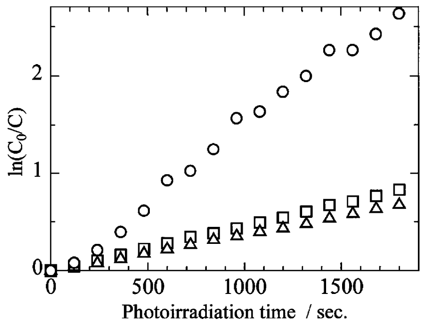


Fig. 8. Basicity dependence of the change of the concentration of rhodamine B with photo-irradiation time for the TIP–TMAOH system. The compositions of the used titanate sols were (TMA^+/TIP, OH^-/TIP) = (0.5, 0.5) (square); (1, 0.5) (triangle); and (1, 1) (circle). The Ti concentration of all the sols was 0.5 M. The concentrations of TMA^+ and OH^- were independently changed using TMAOH and TMABr.

An influence of the basicity of the titanate sol on the photocatalytic reduction of rhodamine B was examined. As mentioned previously, the photo-fading rate of rhodamine B increased in the following order: TIP–TEOA < TIP–NEt_3 < TIP–TMAOH. The pH values of the titanate sols of the TIP–TMAOH, TIP–NEt_3, and TIP–TEOA systems were 13.9, 11.3, and 9.4, respectively. It is inferred that the photo-fading rate of the rhodamine B increased as the basicity of the titanate sol becomes stronger. Accordingly, in order to examine the influence of the basicity of the titanate sol in a further detail, the following three titanate sols of the TIP–TMAOH system were prepared; the first was the sol containing 0.25 M of TMAOH, the second was one containing 0.25 M of TMAOH and 0.25 M of $(CH_3)_4NBr$ (TMABr), and the third was one containing 0.5 M of TMAOH. As the TIP concentration of all these sols was 0.5 M, the compositions of these sols were (TMA^+/Ti, OH^-/Ti) = (0.5, 0.5), (1, 0.5), and (1, 1), respectively. As mentioned in Section 1, in the TIP–TMAOH system, the size and composition of the titanate colloid was not changed in the range of TMA^+/TIP = 0.4–1.0. Thus, it is likely that for these sols, the increase in the added amount of TMAOH had no influence on the concentration of the titanate colloid particle, and led to the increase in the OH^- concentration in the sol. Fig. 8 shows the relation between $\ln(C_0/C)$ and photoirradiation time for the titanate sols with the compositions of (TMA^+/Ti, OH^-/Ti) = (0.5, 0.5), (1, 0.5), and (1, 1). The relation of the fading rate with the (TMA^+/Ti, OH^-/Ti) composition was as follows: (0.5, 0.5) ≈ (1, 0.5) < (1, 1). This result indicates that the increase in the OH^- concentration accelerated the photo-fading, while the TMA^+ concentration had no influence on the fading rate. Next, it is necessary to consider the reason why the OH^- concentration accelerated the photo-fading. It was mentioned previously that the transient semireduced radical, which exhibited the absorption around 420 nm, occurred in the reduction of rhodamine B, and was easily oxidised with the dissolved oxygen. Krüeger and Memming reported that the transient species is much more stabilised with increase in the pH value of a rhodamine B aqueous solution [36]. Therefore, it is inferred that the increase in the OH^- concentration led to the stabilisation of the transient species, resulting in the oxidation of the transient species with the co-existing dissolved oxygen being suppressed.

3.3. Change in the absorption edge of the titanate colloid by the photoirradiation

The photoirradiation to the titanate sol led not only to the decrease of absorbance at the λ_{max} of rhodamine B but also to the appearance of the new absorption in the wavelength between 320 and 450 nm, as shown in Fig. 1. The reason why the new absorption appeared, should be also examined. It was clearly seen from Figs. 1, 3 and 4 that the intensity of the new absorption increased faster when the concentration of the dissolved oxygen was higher. For the titanate sols of the TIP–TMAOH system with the different (TMA^+/Ti, OH^-/Ti) compositions, the increase in the intensity of the new absorption was independent on both the concentrations of TMA^+ and OH^-, although this result is not shown in this paper. Thus, only the concentration of the dissolved oxygen influenced the increase in the intensity of the new

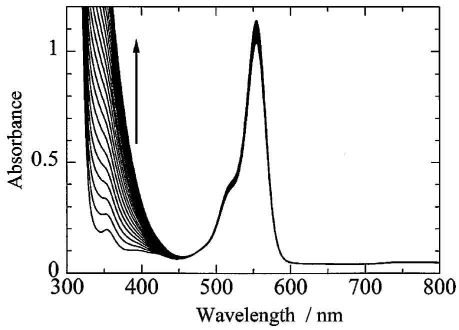


Fig. 9. Influence of the intentional addition of H_2O_2 on the UV-Vis spectra of the titanate sol containing rhodamine B in the TIP–TMAOH system. The concentration of H_2O_2 was changed from 0 to 1 mM.

absorption. These results may indicate that the formation of ${O_2}^{2-}$ ion via the reduction of the dissolved oxygen, $O_2 + 2e^- \rightarrow O_2^{2-}$ contributed to the appearance of the new absorption. Accordingly, a change in the UV-Vis spectra by an intentional addition of H_2O_2 into the titanate sol was investigated, and this result for the TIP–TMAOH system is shown in Fig. 9. This addition of H_2O_2 led to the increase in absorbance in the wavelength ranging between 320 and 450 nm. Further, for the sol after the photoirradiation, the presence of H_2O_2 was confirmed using the oxidation reaction of iodide ion, i.e. $2I^- + H_2O_2 \rightarrow I_2 + OH^-$. After the photoirradiated sol was acidified with an HCl aqueous solution, an aqueous KI solution was added into the sol. For the photoirradiated sols of the TIP–TMAOH and TIP–NEt_3 systems, the addition of the KI solution led to the change in the colour of the sol to yellow, indicating that I_2 was formed by the previously mentioned reaction between H_2O_2 and I^-. Consequently, it was suggested that the H_2O_2 molecules, which were formed by the reduction reaction of the dissolved oxygen, may be adsorbed onto the Ti species, resulting in the peroxotitanate species, and that the absorption in the wavelength ranging between 320 and 450 nm may be due to the peroxotitanate. Although the formation of the peroxotitanate species means a change of the surface state of the titanate colloid, the rate constant of the fading was not changed within the experimented photoirradiation period. This might be attributed to a small amount of the formed H_2O_2, or to a difference of the active site of the photocatalytic reaction from the adsorption site of ${O_2}^{2-}$.

3.4. *Photocatalytic oxidation reaction with the titanate sol*

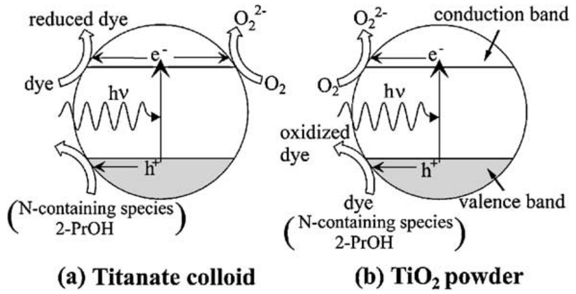
An influence of the photocatalytic oxidation reaction on the fading of rhodamine B was examined. It is likely that in the titanate sols used, the N-containing species, such as TMA^+, NEt_3, and TEOA, and 2-PrOH, which is liberated from TIP via the hydrolysis, act as an electron donor, which can be oxidised photocatalytically, because an N-containing species and an alcohol are usually used as a sacrificial agent for a hydrogen generation by the photocatalysis of a Pt/TiO_2 composite. However, the TMA^+ concentration in the TIP–TMAOH sol had no influence on the fading of rhodamine B, as mentioned previously. Although the 0.5 M TIP–TMAOH sol included 2 M of 2-PrOH, the photoirradiation to the sol with the further intentional addition of 2-PrOH, whose 2-PrOH concentration was 4 M, was also conducted. The increase in the 2-PrOH concentration from 2 to 4 M led only to the slight increase in the fading rate from 1.5×10^{-3} to $1.7 \times 10^{-3}\,s^{-1}$. Thus, both the concentrations of TMA^+ and 2-PrOH had little influence on the photo-fading rate of rhodamine B, indicating that the photocatalytic oxidations are not the rate-determining process in the photocatalysis of the titanate sol, because of the high concentrations of TMA^+ and 2-PrOH. Although the OH^- ion can be also oxidised via the following reaction: $2OH^- + 2h^+ \rightarrow H_2O_2$, in the photoirradiation to the titanate sols of the TIP–TMAOH system with the different (TMA^+/Ti, OH^-/Ti) compositions, the amount of the formed peroxotitanate species was independent on the OH^- concentration, as mentioned previously. This may indicates that the contribution of OH^- to the photocatalytic oxidation was very small.

3.5. *Use of methylene blue instead of rhodamine B*

In order to examine the influence of the type of dye on the photocatalysis of the titanate sol, methylene blue was used instead of rhodamine B. When the photoirradiation under the N_2 gas bubbling was conducted for 4 min, the colour of methylene blue disappeared completely. However, after both the photoirradiation and the N_2 bubbling were stopped, the colour of methylene blue reappeared. This may indicate that methylene blue was photocatalytically reduced with the titanate colloid, and when the irradiation was stopped, the reduced species was oxidised with the dissolved O_2. Although the thorough investigation could not be carried out because of the easy oxidation of the reduced species with the dissolved O_2, it was found that the photocatalytic reduction with the titanate colloid occurred also for methylene blue.

4. Conclusions

The transparent titanate aqueous sol prepared in this study, photocatalytically led to the colour fading of the dyes. The photocatalytic reactions were shown schematically in Fig. 10(a). The photoirradiation under the N_2 bubbling led to the increase in the fading rate of rhodamine B, whereas that under the O_2 bubbling led to the decrease, indicating that the fading reaction competed with the reduction of the dissolved oxygen. In other words, rhodamine B was photocatalytically reduced with the titanate sol. The fading rate was influenced also by the concentration of hydroxide ion in the titanate sol, indicating that the transient semireduced radical of rhodamine B may be stabilised with hydroxide ion, resulting in the oxidation of the transient radical with



(a) Titanate colloid **(b) TiO_2 powder**

Fig. 10. Schematic diagrams of the photocatalyses of: (a) the titanate sol, and (b) the TiO_2 powder.

the coexisting dissolved oxygen being suppressed. On the other hand, the photocatalytic colour fading of rhodamine B with a representative photocatalyst, TiO_2 powder, was accelerated and decelerated by the O_2 and N_2 bubbling, respectively. This tendency shows that rhodamine B was oxidised photocatalytically with the TiO_2 powder. The difference in the photocatalytic reactions between the titanate sol and the TiO_2 powder may be due to the interaction between the titanate colloid and the dye, which enabled the dye to be reduced easily.

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