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Influences of C_1–C_3 Alcohols and Purities of TiO_2 Powders on Their Photoluminescence Properties at Room Temperature

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We have investigated the photoluminescence (PL) of rutile and anatase TiO_2 powders at room temperature in vacuum, in air, and in air with one of C_1–C_3 alcohols (methanol, ethanol, 1-propanol, and 2-propanol). For rutile TiO_2 powder, we observed that the PL intensities in these atmospheres, except air, increase linearly with the square root of the UV irradiation time ($t^{0.5}$), and found that the time dependence agrees with that of the integrated amount of photo-desorbed O_2 from rutile TiO_2 powder. By considering the O_2 photo-desorption and its effect on the surface band bending of the powder, we could explain the time dependence of the PL intensities. This explanation is supported by the experimental results. For anatase TiO_2 powder, the PL intensities in air with one of the alcohols, except for methanol, did not increase linearly with $t^{0.5}$, although those in vacuum and in air with methanol did increase. This inconsistency is probably due to the difference between the photocatalytic activities of anatase TiO_2 powder for the alcohols. In addition, it was found that the difference between the slopes of the PL intensities of the TiO_2 powders in vacuum against $t^{0.5}$ corresponds to that between the purities of the powders.

Recently, extensive studies have been carried out with TiO_2 photocatalysts;[1–3] however, the relationship between the photocatalytic (PC) reaction on TiO_2 and its photoluminescence (PL) properties is not fully understood. So far, it has been reported that the PL wavelength of TiO_2 depends on its particle size[4] and its crystal structure,[5,6] and that the PL intensity of TiO_2 depends on the dopants,[6–9] annealing temperatures,[9–12] atmospheres,[13–17] atmospheres at annealing,[5] and the ambient temperature for the PL measurements.[6,9,18] Anpo et al. have qualitatively explained the dependence of the PL intensity of TiO_2 on its atmosphere by considering the change in the surface band bending.[16] Moreover, a few studies have been made on the relationship between the PC reaction on TiO_2 and its PL properties.[15,19,20] Anpo and Che have recently reviewed applications of PL techniques in relation to photocatalysis and so forth.[21] Nevertheless, little is known about the PL properties of TiO_2 in air at room temperature, although these conditions are the most general for a gas-phase PC reaction and, consequently, a comprehensive understanding of the relationship under the conditions is still lacking. If the relationship can be clarified, the analysis of the PL properties of TiO_2 will become useful for monitoring some changes in the surface conditions associated with the PC reaction, for evaluating the PC activity of TiO_2, and for more thoroughly understanding the mechanisms of TiO_2 photocatalysis. It is therefore important to investigate the PL properties of TiO_2 at room temperature in air with and without a reactant, such as ethanol, for which the mechanisms of the gas-phase PC reaction have been proposed.[22,23] Along these lines, the PL of rutile and anatase TiO_2 powders was measured at room temperature in vacuum, in air, and in air with one of C_1–C_3 alcohols (methanol, ethanol, 1-propanol, and 2-propanol). For rutile TiO_2 powder, we found that the PL intensities in these atmospheres, except in air, increase linearly with the square root of the UV irradiation time ($t^{0.5}$). For anatase TiO_2 powder, the PL intensities in air with one of the alcohols, except for methanol, did not increase linearly with $t^{0.5}$, although those in vacuum and in air with methanol did increase. The results for ethanol agreed with those recently reported by us using several rutile and anatase TiO_2 powders.[24] We have explained these time dependences of the PL intensities. In addition, the influences of the purities of the TiO_2 powders on their PL properties and the PL spectra of the TiO_2 powders in air at room temperature are discussed.

Experimental

Anatase and rutile TiO_2 powders were purchased from Aldrich (Aldrich-A and Aldrich-R), Kanto Chemical Co. (Kanto-A and Kanto-R), and Wako Pure Chemical Ind. (Wako-A and Wako-R). They were used as received. Reagent-grade alcohols (methanol (Kanto Chemical Co.), ethanol (Amakasu Chemical Ind.), 1-propanol, and 2-propanol (Wako Pure Chemical Ind.)) were used without further purification. To calculate the crystalline composition and the primary particle size of the TiO_2 powder, X-ray diffraction was measured with a Rigaku Rint 2000 X-ray diffractometer. The PL of the TiO_2 powder was measured at room temperature on a Shimadzu RF5300PC spectrofluorophotometer equipped with filters (U-340 and UV-39) to eliminate the stray light from the spectroscope and the scattered light from the powder. The excitation wavelength was 335 nm. The time-courses of the PL intensities of the TiO_2 powders were measured at a PL wavelength of 500 nm. The TiO_2 powder was set in a holder by pressing it with a glass plate. The holder was placed in a cylindrical stainless-steel cell with two optical windows. The cell was connected to a vacuum system, inside of which the pressure, measured with a Pirani gauge, was 1 Pa. The TiO_2 powder was outgassed under vacuum for 60 min before a PL measurement in vacuum, while it was exposed to an alcohol vapor in the dark for 60 min to attain adsorption equilibrium before a PL measurement in air with the alcohol. To evaluate the PC activities of the TiO_2 powders, PC reactions of methanol and ethanol using the powders were carried out under UV irradiation with 8 tubes of black lights (Toshiba FL20S-BLB 20W) in a batch reactor, in which the concentrations of methanol and ethanol in the reactions were measured by Fourier-transform infrared spectroscopy (Nicolet 800).

Results and Discussion

Crystallite Properties. Table 1 shows that the rutile TiO_2 powders had a substantially rutile structure (> 95%) and that the anatase TiO_2 powders had a substantially anatase structure (> 96%). Thus, the effects of the crystal structure of TiO_2 powder on its PL can be examined by comparing the PL properties of the rutile TiO_2 powders and those of the anatase TiO_2 powders. The primary particle sizes of the TiO_2 powders were very close to one another, as shown in Table 1, and hence we neglected the difference between the influences of the primary particle sizes on the PL and on the PC reaction.

PL Spectra in Air. Figure 1 shows the PL spectra of the TiO_2 powders in air. The PL spectra of the anatase TiO_2 powders and Aldrich-R were broad bands at about 500 nm, which were the same bands as those in vacuum and in air with ethanol. In contrast, the PL spectra of Kanto-R and Wako-R showed two low broad bands at about 450 nm and about 500 nm, while in air with ethanol vapor and in vacuum the PL spectra were broad bands at about 500 nm, similar to those of the other powders. Thus, we measured the PL intensity at 500 nm to observe its change with time. The PL of anatase and rutile TiO_2 have been interpreted as emissions from self-trapped excitons and free excitons, respectively.[6] This difference in the exciton type was thought to be a reason for the difference in PL spectra between the anatase TiO_2 powders and the rutile TiO_2 powders. The spectra of Aldrich-R, however, contradicts the above idea. Another cause of the difference in the PL spectra between the two powders (Kanto-R and Wako-R) and the other powders seems to be the effect of impurities in the TiO_2 powders, because the TiO_2 purity of Aldrich-R (99.99%) is much higher than that of the two powders (> 99.0%). It was reported that the addition of impurities usually increases the probability of nonradiative transitions, and thereby the PL intensity decreases remarkably compared to that of pure samples.[8] This effect of impurities in the two powders on their PL may be revealed obviously in air.

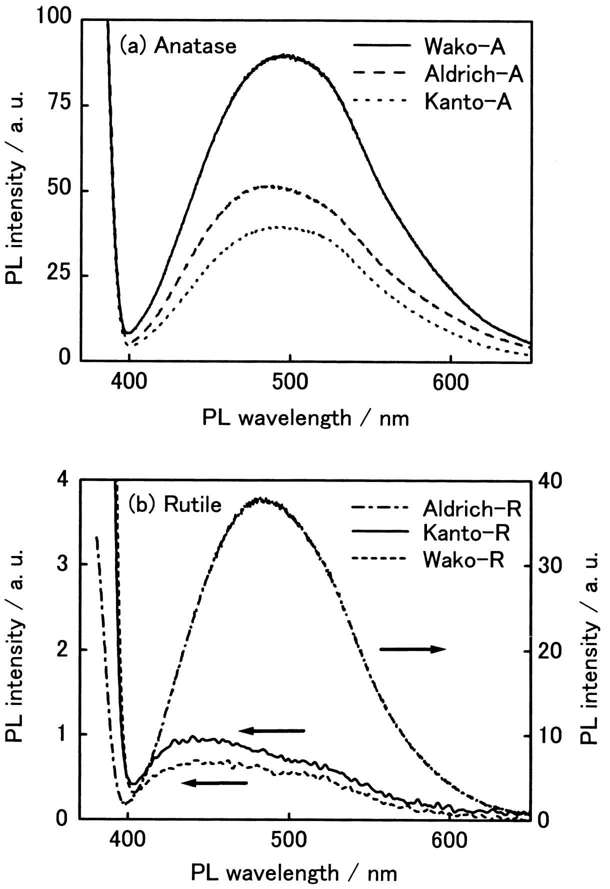

Fig. 1. The photoluminescence (PL) spectra of the anatase (a) and the rutile (b) TiO_2 powders in air at room temperature.

The PL of the TiO_2 powders differed from one another in wavelength and intensity (Fig. 2). The differences in their PL intensities were large. For example, the PL intensity of Wako-A was about 100-times those of Kanto-R and Wako-R. These differences show that the PL of TiO_2 reflects many of the factors mentioned in the introduction, and suggest that TiO_2 pow-

Table 1. The Crystallite Properties of the TiO_2 Powders

TiO_2 powder		Purity /%	Anatase percentage /%a)	Primary particle size /nmb)
Rutile	Aldrich-R	99.99	4	63
	Kanto-R	> 99.0c)	0	58
	Wako-R	> 99.0	3	51
Anatase	Aldrich-A	> 99.9	97	54
	Kanto-A	> 98.0d)	100	54
	Wako-A	> 98.5	99	54

a) Calculated with the equation: anatase percentage (%) = $100/(1 + 1.265\, I_R/I_A)$, where I_R and I_A represent the X-ray diffraction intensities of the rutile peak at 2theta = 27.4 deg and the anatase peak at 2theta = 25.3 deg, respectively.[25] b) Calculated from the peak broadening of the X-ray diffraction using Scherrer's equation. c) Cl, NO_3, PO_4, SO_4, Fe, and Pb are included as impurities. d) SO_4, Pb, and Fe are included as impurities.

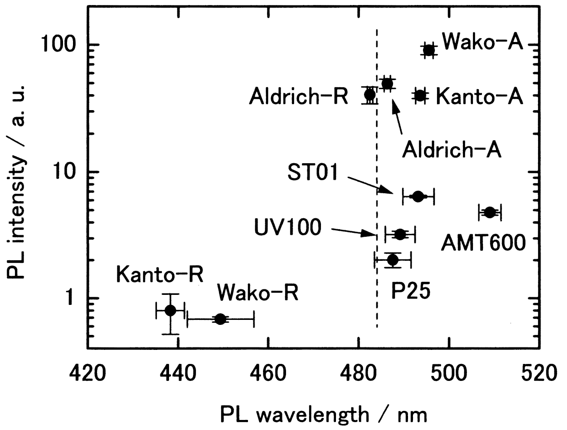

Fig. 2. The photoluminescence (PL) wavelengths and intensities of the TiO_2 powders in air at room temperature. The error bars represent standard deviations. The dotted line at about 485nm represents the boundary between the PL wavelengths of the rutile TiO_2 powders and those of the anatase ones.

ders have different PL spectra, depending on their preparation. Other anatase TiO_2 powders (P25 (Nippon Aerosil), AMT600 (Tayca), UV100 (Sachtleben Chemie), and ST01 (Ishihara Sangyou)) also had different PL wavelengths and PL intensities (Fig. 2). We did not study the four powders further because their primary particle sizes were different from those of the 6 powders used in this study; those of UV100 and ST01 were 9 nm[25] and those of P25 and AMT600 were about 20 nm. We could thus identify 10 commercial TiO_2 powders by their PL spectra in air at room temperature. This finding indicates that PL spectroscopy is useful for identifying TiO_2 powders.

Time-Courses of the PL Intensities of Rutile TiO_2 Powder. The PL intensities of rutile TiO_2 powder Kanto-R were measured in air with the C_1–C_3 alcohols at room temperature; we found that the PL intensities in these atmospheres increase linearly with $t^{0.5}$ (Fig. 3). The plots of the PL intensities against $t^{0.5}$ agree very well with their regression lines; the squares of the regression coefficients were more than 0.98. These results correspond to the fact[26] that the amount of photodesorbed O_2 from rutile TiO_2 powder decreases with time, and that the integrated amount of the desorbed O_2 increases linearly with $t^{0.5}$. This time dependence is attributed to the recombination of electrons of chemisorbed O_2 on the TiO_2 surface with the photo-generated holes.[26,27] The results for ethanol agree with a recent report concerning the rutile and anatase TiO_2 powders.[24] We have explained the time dependence of the PL intensities of rutile TiO_2 powder in air with the alcohols by considering the O_2 photo-desorption and its effect on the surface band bending of the powder,[16] as follows: adsorbed O_2 on the rutile TiO_2 powder is photo-desorbed by the excitation light for the PL measurement. Instead, the alcohol is adsorbed and inhibits O_2 from being re-adsorbed on the powder. This substitution diminishes the surface charge density of the powder (N_s) linearly with $t^{0.5}$ (Eq. 1),[27]

$$N_s = A - Bt^{0.5} \quad (A, B\text{: Const}), \tag{1}$$

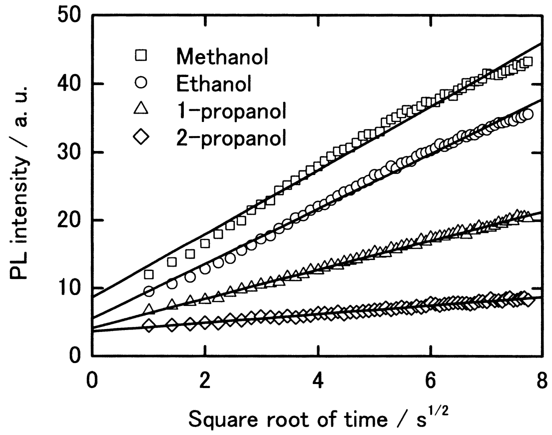

Fig. 3. The relationships between the photoluminescence (PL) intensities of rutile TiO_2 powder Kanto-R in air with C_1–C_3 alcohols (methanol, ethanol, 1-propanol, and 2-propanol) and the square root of the UV irradiation time from 1 s to 60 s. The squares of the regression coefficients are more than 0.98.

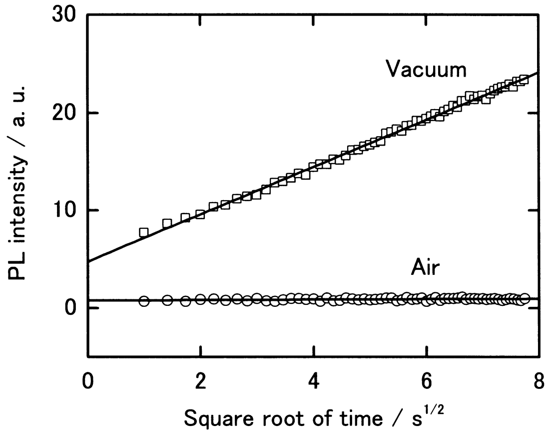

Fig. 4. The photoluminescence (PL) intensities of rutile TiO_2 powder Kanto-R in vacuum and in air vs the square root of the UV irradiation time from 1 s to 60 s.

and decreases the thickness of the space-charge layer linearly with $t^{0.5}$. This decrease enhances the electron-hole recombination at the powder's surface because of the decrease in thickness of the charge separation region where no electron-hole recombination occurs. Thus, the PL intensity increases with the decrease, i.e., linearly with $t^{0.5}$. If the above model is correct, the PL intensity in vacuum is expected to increase linearly with $t^{0.5}$. Figure 4 shows that the PL intensity in vacuum increased as expected, while that in air remained unchanged. The PL wavelength in vacuum was 487 nm; those in air with methanol, ethanol, 1-propanol, and 2-propanol were 491 nm, 491 nm, 491 nm, and 488 nm, respectively. The experimental uncertainties associated with these PL wavelength measurements were ca. 0.4%. Within the uncertainties, the PL wavelength in vacuum agrees with that in air containing one of the alcohols. Thus, the mechanism of the PL in vacuum seems to be identical with that in air with one of the alcohols. These results support our model. Moreover, it is presumed from our

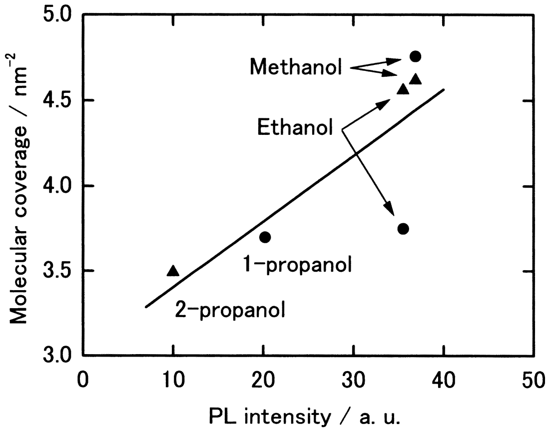

Fig. 5. The molecular coverages of methanol, ethanol, 1-propanol, and 2-propanol on rutile TiO_2 powder reported in Refs. 28 (circle) and 29 (triangle) were plotted against the photoluminescence (PL) intensities of rutile TiO_2 Kanto-R in air with these alcohols at room temperature of this study.

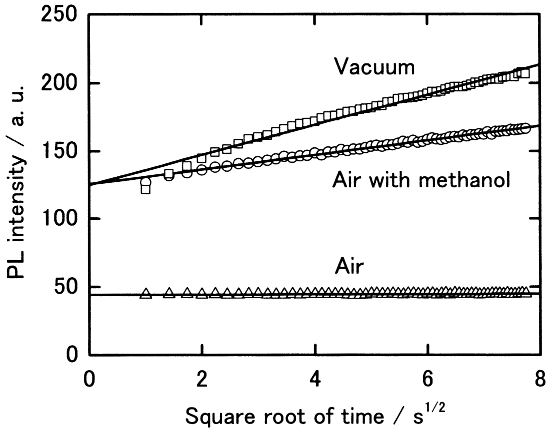

Fig. 6. The photoluminescence (PL) intensities of anatase TiO_2 powder Kanto-A in vacuum, in air with methanol, and in air vs the square root of the UV irradiation time from 1 s to 60 s.

model that the higher adsorption of alcohol on TiO_2 powder increases the PL intensity of the powder because the larger amount of alcohol occupies the sites on which O_2 were adsorbed before UV irradiation. The order of the molecular coverages of the alcohols on rutile TiO_2 powder was reported to be methanol > ethanol > 1-propanol > 2-propanol[28,29] and, as presumed, this order agreed with that of the PL intensities in air with the alcohols (Fig. 5). This result also supports our model.

Time-Courses of the PL Intensities of Anatase TiO_2 Powder. Figure 6 shows the time-courses of the PL intensities of anatase TiO_2 powder Kanto-A in vacuum, in air, and in air with methanol. We found that the PL intensities in vacuum and in air with methanol increase linearly with $t^{0.5}$, while in air without methanol they remain unchanged. On the contrary, the PL intensities in air with ethanol, 1-propanol, and 2-propanol decreased quickly for a few seconds at the beginning, and then increased very slowly (Fig. 7) compared with those in vacuum and in air with methanol. The result for ethanol agrees with the results recently reported by us using the anatase TiO_2 powders.[24] The proposed model discussed in the previous section is inapplicable to the PL intensities of the anatase TiO_2 powder in air with the alcohols, except for methanol. This inconsistency is likely to be due to the difference between the PC activities of the anatase TiO_2 powder for the alcohols because of our result that the half-life of methanol in the PC reaction using the powder was about three-times larger than that of ethanol. The difference between the activities for methanol and ethanol agrees with that reported earlier.[30] Thereby, the influence of the PC oxidation of the alcohols, except for methanol, on the PL of anatase TiO_2 powder is thought to be much stronger than that of rutile TiO_2 powder, while the influence of the PC oxidation of methanol on the PL of anatase TiO_2 powder seems not to be very strong. In general, the PC activity of anatase TiO_2 is higher than that of rutile TiO_2. Indeed, in an experiment of PC oxidation of ethanol using the TiO_2 powders, the half-life of ethanol with Kanto-A was less than one-fifth of that with Kanto-R. Thus, the anatase TiO_2 powder, which has a much higher PC activity than the rutile TiO_2 powder, would oxidize alcohol immediately and consume photo-excited electrons and holes in the powder. Moreover, this rapid oxidation would increase the possibility of O_2 adsorption on the powder. These considerations suggest that the PC reaction decreases the PL intensity of the anatase TiO_2 powder, and that they are applicable to the PL intensities in air with the alcohols, except for methanol. In air with methanol, the PC activity of the anatase TiO_2 powder for methanol is probably not high enough to suppress an increase in the PL intensity, and thus the PL intensity increases linearly with $t^{0.5}$, even under the PC reaction. The decrease at the beginning (Fig. 7) can be explained by considering the change in the surface band bending of the anatase TiO_2 powder as follows: at the beginning of the PL measurement, photo-excited electrons are accumulated on the TiO_2 surface because photo-induced holes are consumed in the PC reactions of ethanol, 1-propanol, and 2-propanol. Consequently, the surface charge density (N_s) increases. In contrast, N_s under the PC reaction of methanol would decrease because of the low PC activity for methanol and the highest absorption ability of metha-

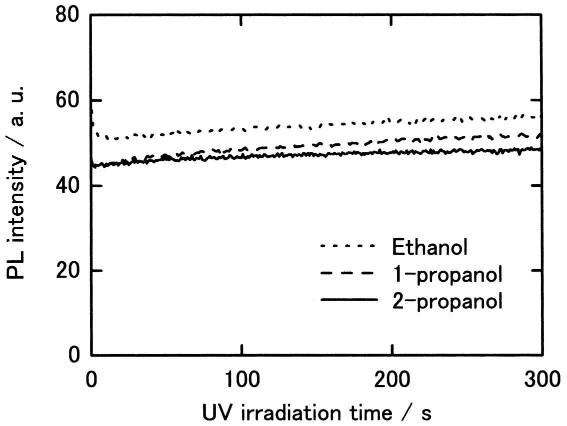

Fig. 7. The photoluminescence (PL) intensities of anatase TiO_2 powder Kanto-A in air with ethanol, 1-propanol, and 2-propanol vs the UV irradiation time.

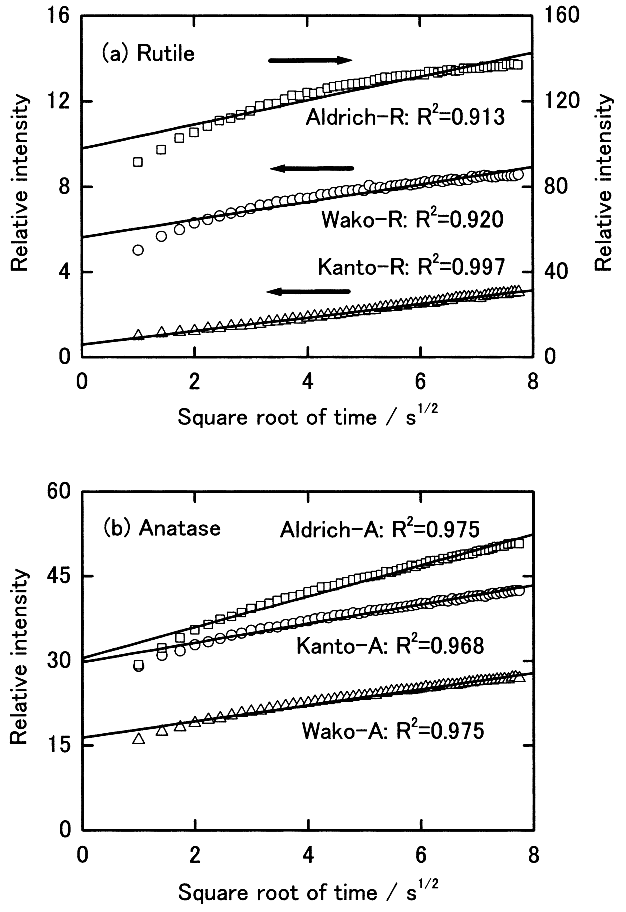

Fig. 8. The photoluminescence (PL) intensities of the rutile (a) and the anatase (b) TiO_2 powders in vacuum at room temperature vs the square root of the UV irradiation time from 1 s to 60 s. The relative intensity is based on the PL intensity of Kanto-R at 1 s as 1.

nol among the alcohols. The increase of N_s enhances the thickness of the space-charge layer, where electron-hole recombination is forbidden, resulting in a decrease of the PL intensity. A few seconds later, the consumption rate of the hole decreases, which diminishes the surface charge density, resulting in an increase of the PL intensity.

It was reported that the higher PC activity of anatase TiO_2 powder with respect to that of rutile TiO_2 powder may be explained by the fact that anatase TiO_2 powder has a higher O_2 adsorption capacity than rutile TiO_2 powder.[31] This is consistent with our explanation for the time-course of the PL intensity. Rutile TiO_2 powder loses adsorbed O_2 quickly via photo-desorption because rutile powder has a lower O_2 adsorption capacity, resulting in a rapid increase of the PL intensity. In contrast, it takes a long time for anatase TiO_2 powder to lose its adsorbed O_2 because of the large amount of adsorbed O_2 and competition between the O_2 photo-desorption and the PC reaction of alcohol.

Influence of Purities of the TiO_2 Powders on the Time-Courses of the PL Intensities in Vacuum. A comparison of the slopes of the regression lines in Fig. 8a shows that the slopes of Kanto-R and Wako-R are nearly the same, while the slope of Aldrich-R is much larger than those of Kanto-R and Wako-R. We found that the difference of the slopes between the TiO_2 powders corresponds to that of the purities between the powders. That is, a comparison of the purities of the rutile TiO_2 powders in Table 1 shows that the levels of the purity of Kanto-R and Wako-R are the same (99%), while the purity of Aldrich-R is much higher than those of the two powders. Even in air with ethanol, the same relation among the three powders was observed as in our previous study.[24] Furthermore, a similar relation between the slopes of the regression lines for the anatase TiO_2 powders (Fig. 8b) and the purities of the powders (Table 1) was observed. These relations suggest that during O_2 photo-desorption, the slope of the plot of the PL intensity for TiO_2 powder against $t^{0.5}$ depends on its purity. They also indicate that the impurities in the powder prevent O_2 photo-desorption by trapping holes or by disturbing the migration of holes to the powder's surface. It appears that the nonradiative electron-hole recombination occurs at the impurities or around them, and that the recombination rate corresponds to the impurity concentration. In contrast, the linearity of the plots against $t^{0.5}$ in Fig. 8 are independent of the purities of the TiO_2 powders. The deviations of the plots for Aldrich-R and Wako-R from the regression lines are larger than those for the other powders. The deviations for these two powders in vacuum are probably due to the saturations of the PL intensities. This effect may be small for Kanto-R because the increase in the PL intensity of Kanto-R is much smaller than those of Aldrich-R and Wako-R. In air with ethanol, as we previously reported, the deviations for these two powders are small; the squares of the regression coefficients for Aldrich-R and Wako-R are 0.997 and 0.990.[24] The PL intensities of these two powders in vacuum are thought to be saturated faster than in air with ethanol.

In conclusion, 1) for rutile TiO_2 powder, we observed that the PL intensities in vacuum and in air with the C_1–C_3 alcohols increase linearly with $t^{0.5}$, and found that the time dependence of the PL intensities agrees with that of the integrated amount of photo-desorbed O_2 from rutile TiO_2 powder. To explain the time dependence, a model supported by the experimental results has been proposed. For anatase TiO_2 powder, we found that the PL intensities in air and in air with one of the alcohols, except for methanol, do not increase linearly with $t^{0.5}$, although those in vacuum and in air with methanol do increase. This inconsistency can be explained by considering the difference between the PC activities for the alcohols. 2) It was found that the difference between the slopes of the PL intensities of the TiO_2 powders in vacuum against $t^{0.5}$ corresponds to that between the purities of the powders. 3) The PL spectra of ten commercial TiO_2 powders in air at room temperature differed from one another in wavelength and in intensity, suggesting that PL spectroscopy is useful for identifying TiO_2 powders.

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References

1 A. Hagfeldt and M. Gratzel, *Chem. Rev.*, **95**, 49 (1995).
2 A. L. Linsebigler, G. Lu, and J. T. Yates, Jr., *Chem. Rev.*,

95, 735 (1995).

3 A. Fujishima, T. N. Rao, and D. A. Tryk, *J. Photochem. Photobiol. C*, **1**, 1 (2000)

4 M. Anpo, T. Shima, S. Kodama, and Y. Kubokawa, *J. Phys. Chem*., **91**, 4305 (1987).

5 S. K. Poznyak, V. V. Sviridov, A. I. Kulak, and M. P. Samtsov, *J. Electroanal. Chem*., **340**, 73 (1992).

6 H. Tang, H. Berger, P. E. Schmid, and F. Levy, *Solid State Commun*., **87**, 847 (1993).

7 M. M. Rahman, K. M. Krishna, T. Soga, T. Jimbo, and M. Umeno, *J. Phys. Chem. Solids*, **60**, 201 (1999).

8 N. Bonini, M. C. Carotta, A. Chiorino, V. Guidi, C. Malagu, G. Martinelli, L. Palialonga, and M. Sacerdoti, *Sens. Actuators, B*, **68**, 274 (2000).

9 K. M. Krishna, M. M. Rahman, T. Miki, T. Soga, K. Igarashi, S. Tanemura, and M. Umeno, *Appl. Surf. Sci*., **113/114**, 149 (1997).

10 W. F. Zhang, M. S. Zhang, Z. Yin, and Q. Chen, *Appl. Phys. B*, **70**, 261 (2000).

11 W. F. Zhang, M. S. Zhang, and Z. Yin, *Phys. Status. Solid. A*, **179**, 319 (2000).

12 T. Sekiya, S. Kamei, and S. Kurita, *J. Lumin*., **87-89**, 1140 (2000).

13 M. Anpo, T. Shima, and Y. Kubokawa, *Chem. Lett*., **1985**, 1799.

14 K. Hashimoto, M. Hiramoto, and T. Sakata, *Proc. Electrochem. Soc*., **88-14**, 395 (1988).

15 M. Anpo, M. Tomonari, and M. A. Fox, *J. Phys. Chem*., **93**, 7300 (1989).

16 M. Anpo, K. Chiba, M. Tomonari, S. Coluccia, M. Che, and M. A. Fox, *Bull. Chem. Soc. Jpn*., **64**, 543 (1991).

17 E. Konstantinova, J. Weidmann, and TH. Dittrich, *J. Porous Mater*., **7**, 389 (2000).

18 L. Forss and M. Schubnell, *Appl. Phys. B*, **56**, 363 (1993).

19 K. Ikeue, H. Yamashita, and M. Anpo, *Chem. Lett*., **1999**, 1135.

20 K. Fujihara, S. Izumi, T. Ohno, and M. Matsumura, *J. Photochem. Photobiol. A*, **132**, 99 (2000).

21 M. Anpo and M. Che, “Advances in Catalysis,” ed by W. O. Haag, B. C. Gates, and H. Knözinger, Academic press (1999), Vol. 44, p. 199.

22 M. L. Sauer and D. F. Ollis, *J. Catal*., **158**, 570 (1996).

23 D. S. Muggli, K. H. Lowery, and J. L. Falconer, *J. Phys. Chem*., **180**, 111 (1996).

24 H. Nakajima, K. Itoh, and M. Murabayashi, *Chem. Lett*., **2001**, 304.

25 Y. Nosaka, M. Kishimoto, and J. Nishino, *J. Phys. Chem. B*, **102**, 10279 (1998).

26 Y. Yanagisawa and Y. Ota, *Surf. Sci. Lett*., **254**, 433 (1991).

27 Y. Shapira, R. B. McQuistan, and D. Lichtman, *Phys. Rev. B*, **15**, 2163 (1977).

28 Y. Suda, T. Morimoto, and M. Nagao, *Langmuir*, **3**, 99 (1987).

29 V. S. Lusvardi, M. A. Barteau, and W. E. Farneth, *J. Catal*., **153**, 41 (1995).

30 W. C. Wu, C. C. Chuang, and J. L. Lin, *J. Phys. Chem. B*, **104**, 8719 (2000).

31 A. Sclafani and J. M. Herrmann, *J. Phys. Chem*., **100**, 13655 (1996).