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Photocatalytic activity of TiO_2 particulate films prepared by depositing TiO_2 particles with various sizes

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TiO_2 particles of various sizes were prepared by grinding in cyclohexanone, and TiO_2 particulate films were obtained by depositing these TiO_2 particles with various sizes onto a glass or quartz substrate. The effect of the particle size and thickness on the photocatalytic properties of the films was evaluated via oxidative degradation of gaseous 2-propanol. The initial rate of 2-propanol degradation under UV light irradiation for the films deposited with 30 nm TiO_2 particles increased with increasing film thickness up to 600 nm, and reached a saturated value above this film thickness. Photocatalytic activity for the films with thickness below 600 nm was larger when smaller TiO_2 particles were deposited onto the substrate, due to the increase in the surface area of the particulate films. Furthermore, saturated values of the photocatalytic activity for thick films were smaller for the films deposited with smaller particles, which is mainly attributed to the change in crystal form of the particles during the grinding treatment.

Keywords: TiO_2, photocatalyst, cyclohexanone, 2-propanol, particle size.

Introduction

When n-type semiconductors such as TiO_2, ZnO, CdS are excited by a photon whose energy is greater than their band gap, an electron from the valence band can be excited to the conduction band, thus creating electron-hole pairs. The electron and hole pairs are then transferred to the surface and can oxidize or reduce surface-adsorbed species. TiO_2, in particular, has beneficial characteristics, such as its physical and chemical stability, as well as the strong oxidizing power of the photo-generated holes, with which most organic compounds can be oxidized to carbon dioxide at ambient temperature and pressure (Fujishima and Honda 1972, Kubokawa *et al.* 1988, Kiyono 1993, Ohko *et al.* 1997). Therefore, the

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photocatalytic degradation of harmful and toxic compounds using TiO_2 powders and films has great promise for the purification of air and water. Furthermore, a passive type photocatalytic purification system for living environments with very weak UV light ($\sim mW \cdot cm^{-2}$) from sunlight and fluorescent lamps has been developed recently with growing interest (Vinodgopal *et al.* 1993, Takeda *et al.* 1995, Ohko *et al.* 1997, Anpo *et al.* 1998).

A particulate thin film generated from colloidal suspensions is one of most promising forms of TiO_2 photocatalysts, since such particulate films retain the photophysical and photochemical properties of individual semiconductor particles and, thus, carry out the photocatalytic reactions with similar high selectivity and efficiency as in particle suspensions (Hoffmann *et al.* 1995). In order to design the TiO_2 particulate film with high photocatalytic activity, it is essential to investigate the effect of particle size and film thickness on the photocatalytic activity. However, difficulty in preparing TiO_2 particles with different particle sizes and identical physical and chemical properties at the same time has prevented studying the effect of particle size on the photocatalytic properties in detail. In this study, TiO_2 particles whose size varied with grinding in cyclohexanone were prepared, and TiO_2 particulate films were obtained by depositing these TiO_2 particles with various sizes onto glass or quartz substrates. The effect of the deposited particle size and thickness on the photocatalytic properties of the films thus obtained were evaluated via oxidative degradation of gaseous 2-propanol.

Experimental

Materials

TiO_2 particles (P-25; 70% anatase, 30% rutile, Nippon-Aerosil Co., Tokyo, Japan) with an average primary particle diameter of 30 nm were used. Cyclohexanone used as the disperse medium was obtained from Wako Pure Chemical Co. (Tokyo, Japan). Analytical grade 2-propanol was purchased from Tokyo Kasei Co. (Tokyo, Japan) and used as received. For the estimation of the surface area of the particulate films, a cyanine dye NK-3422 (1-(2-carboxyethyl)-2-[7-[1-(2-carboxyethyl)-1,3-dihydro-3,3-dimethyl-2H-indol-2-ylidene]-1,3,5-heptatrienyl]-3,3-dimethyl-3H-indolium hydroxide, inner salt, Nippon Kankoh-Shikiso Kenkyusho Co., Ltd, Tokyo, Japan) was used.

Preparation of TiO_2 suspensions

Suspensions of TiO_2 (Jinbo 1989, Nakamura 1989, Komuro *et al.* 1994) were prepared by suspending 2 wt% of P-25 powder in cyclohexanone. Continuous grinding was performed in a satellite type ball mill (Type P-7, Frich Co., Ltd.) with yttria-stabilized zirconia balls for 5, 15 and 48 h. Rotation speed and revolution radius were 750 rpm and 10 cm, respectively. TiO_2 particles, after various hours of grinding, were used for the following film preparation process.

Preparation of TiO_2 particulate films

TiO_2 particulate films were prepared onto the glass or quartz substrate by dipping the substrate vertically into the TiO_2 suspensions with a speed of 50 mm/

min, followed by calcination for 1 h at 450 °C. Film thickness was controlled by varying the number of dipping treatments.

Particle size measurement

Particle size of TiO_2 powders was measured with a dynamic light scattering technique using a 4700-type submicron-meter particle analyser (Malvern Instruments Ltd, UK), with a multibit 8 Malvern correlator with delayed channels. The light source was an argon laser (Coherent Co., Innova 90) with a wavelength of 488 nm and a power of 5 W, and the time-dependent correlation function of the scattered light intensity was measured at a scattering angle of 90°.

Characterization of TiO_2 particulate films

Formation of the TiO_2 particulate films was confirmed by UV-vis absorption spectroscopy (Shimadzu Co., Model MPS-2000). Measurement of film thickness was carried out by a cross-sectional observation of the samples embedded in epoxy resin using a scanning electron microscope (SEM, Mode S-510, Hitachi Co.). The microstructure of the surface of the particulate films was observed with atomic force microscope (AFM, Model SPI3800, Seiko Instruments Co.) using the tapping mode.

The surface area of the particulate films was evaluated from the adsorbed amount of cyanine dye NK-3422 on the film surface. The amount of NK-3422 was calculated from the absorption at 746 nm. The crystal form of the ground and unground TiO_2 powders loaded on the substrate was analysed by X-ray diffractometer (Rigaku Co., Tokyo, Japan) with high intensity FeKα radiation.

Measurement of photocatalytic activity

The photocatalytic activities of the TiO_2 films were evaluated by the oxidative degradation of gaseous 2-propanol. UV light (<400 nm) from a 200 W Hg-Xe lamp (Supercure-203S, San-ei Co., Osaka, Japan) was used for excitation of the films. The 2-propanol concentration was measured using a GC (Model GC-8A, Shimadzu Co., Kyoto, Japan) equipped with a 3-m PEG1000 column and a flame ionization detector, using N_2 as a carrier gas.

The initial reaction rate was calculated from the concentration change of 2-propanol immediately after the UV light irradiation and these values were used as an indicator of photocatalytic activity. The reasons that 2-propanol was chosen as a reactant for these experiments were that (*i*) it is efficiently photodecomposed to acetone, which undergoes further reactions at a much slower rate, (*ii*) a single photon is considered to participate in the generation of each acetone molecule, and (*iii*) its self-oxidation is negligible.

Results and discussion

Effect of grinding in cyclohexanone on the size of TiO_2 particles

In this study, the particle size of TiO_2 deposited onto the substrate was controlled by grinding treatment of the suspension using a planet type ball mill. Suspensions with high dispersibility were obtained after milling treatment in cyclohexanone. The average particle size of TiO_2 particles before the treatment

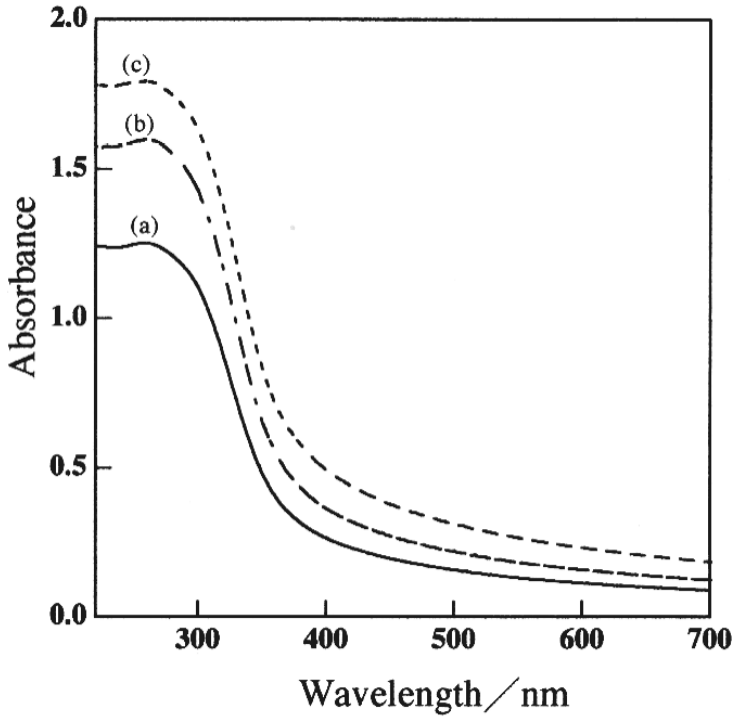


Figure 1. UV-Vis absorption spectra of TiO_2 particulate films deposited on quartz substrates (size of deposited particles: 70 nm, number of dipping, (*a*) 1, (*b*) 3, (*c*) 5).

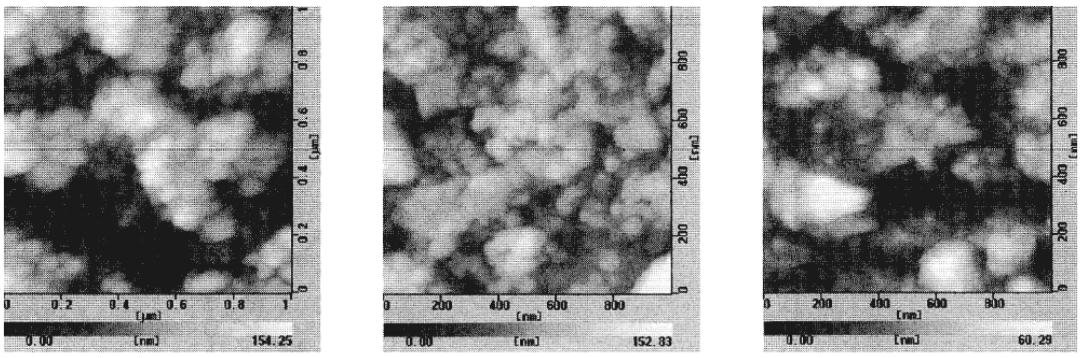
was 140 nm due to aggregation of primary size particles, while particle size decreased to 110, 70, 30 nm after grinding with the planet type ball mill for 5, 15 and 48 h, respectively. It should be noted that the particle size after 48 h treatment (30 nm) was almost identical to the primary particle size of P-25.

Physical and chemical properties of particulate films

TiO_2 particulate films were prepared by depositing the TiO_2 particles obtained onto quartz substrates. Figure 1 shows UV-visible absorption spectra of particulate films obtained by dipping the substrate at various times into the suspension grinding-treated for 15 h (average particle size 70 nm). A broad absorption peak below 400 nm, corresponding to the band gap energy of TiO_2 (=3.1 eV), was observed (Kiyono 1993), indicating the formation of TiO_2 particulate films.

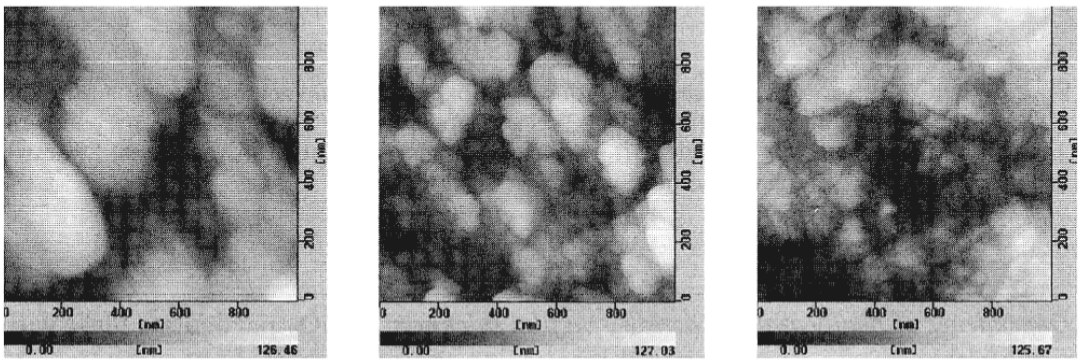
The absorption peak increased almost linearly with an increasing number of dipping. Linear dependency of film thickness on dipping number was also confirmed by cross-sectional observation using SEM. These results show that the film thickness is controllable by numbers of dipping. Similar results were also obtained when TiO_2 suspensions with different particle size were deposited.

The surface structure of the particulate films was observed using AFM, in order to examine the effect of grinding and calcination. Figures 2 and 3 show the surface morphology of the glass substrate dip-coated with TiO_2 suspension before and after calcination at 450 °C for 1 h. The scan area is 1 × 1 μm in all figures. The size of TiO_2 particles deposited onto the substrate decreased with increasing length of milling treatment. In addition, the loaded particle size slightly increased after calcination, as shown in figure 3, due to the aggregation of the particles (Montoya *et al.* 1992, Komiyama *et al.* 1995). The tendency that particle size



(*a*) (*b*) (*c*)

Figure 2. AFM images of TiO_2 particulate films before heat treatment. Grinding treatment of TiO_2 particles, (*a*) 5 h, (*b*) 15 h, (*c*) 48 h.



(*a*) (*b*) (*c*)

Figure 3. AFM images of TiO_2 particulate films after heat treatment at 450 °C for 1 h. Grinding treatment of TiO_2 particles, (*a*) 5 h, (*b*) 15 h, (*c*) 48 h.

decreased with increasing length of grinding treatment was preserved, even after calcination.

Effect of film thickness on photocatalytic activity

Photocatalytic reactions on the TiO_2 particulate films. Photocatalytic activity of the TiO_2 particulate films was evaluated through oxidative degradation of 2-propanol under UV light irradiation. The initial concentration of 2-propanol in a 300 ml cell with quartz window was 2.1 μmol/m^3. The 2-propanol concentration was monitored with GC in the dark for 2 h at 30 °C, followed by monitoring under UV light irradiation (2.3 mW/cm^2) for 2 h.

The results obtained using the film deposited with 70 nm TiO_2 particles and of 280 nm film thickness are shown in figure 4. The decrease in 2-propanol concentration and formation of acetone were observed under UV light irradiation. The initial degradation rate of 2-propanol was calculated from the slope in figure 4 immediately after light irradiation.

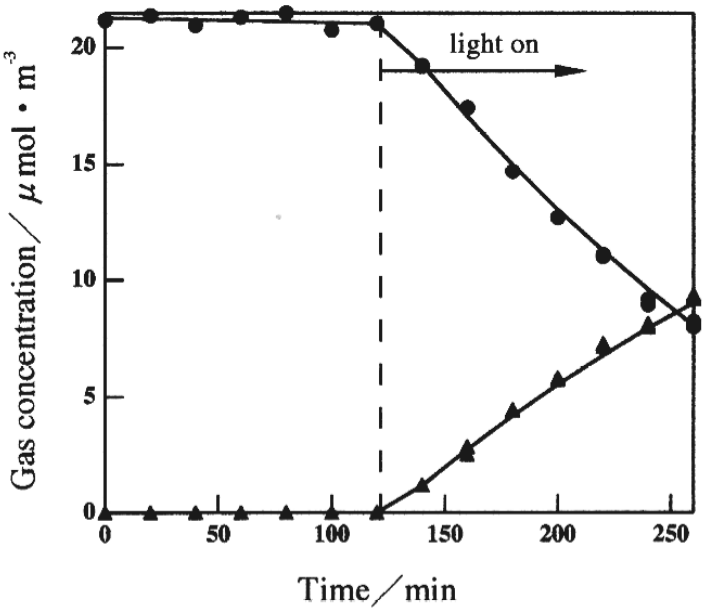


Figure 4. Concentration changes in gaseous 2-propanol (●), and acetone (▲) as a function of time in the decomposition of gaseous 2-propanol. The TiO_2 film was prepared by depositing the TiO_2 particles after 15 h grinding treatment (film thickness, 290 nm). Incident UV intensity; 2.3 mW cm^{-2}.

Dependence of photocatalytic activity on film thickness. TiO_2 particulate films with various thicknesses were prepared by varying the number of dipping treatments and the effect of film thickness on the photocatalytic activity was studied. The initial rate of 2-propanol degradation was calculated for each film and plotted against film thickness. Figure 5 represents the results obtained for the film deposited with 30 nm TiO_2 particles (48 h grinding). The initial degradation rate increased almost linearly with increasing film thickness below 600 nm, while it reached a certain saturated value above this film thickness, as shown in figure 5.

Photocatalytic reactions are generally initiated by photogenerated holes (or electrons) attacking the surface-adsorped species. Therefore, the irradiated area of surface to which 2-propanol can adsorb is one of the important factors that determine the photocatalytic activity. The intensity of irradiated UV light and the degree of its absorption in the film also affected photocatalytic activity. Furthermore, charge separation efficiency of photo-generated holes and electrons, i.e. density of photo-generated holes on the film surface, is another important index of photocatalytic activity (Kubokawa *et al.* 1988). Accordingly, the following three possibilities may be considered as causes why photocatalytic activity reaches the saturated value above a certain thickness.

(1) Saturation of surface area of the particulate film above a certain film thickness;
(2) Retardation of UV light transmission due to absorption and
(3) Promotion of recombination between holes and electrons in thick films.

The contribution of each cause above will be discussed in the following.

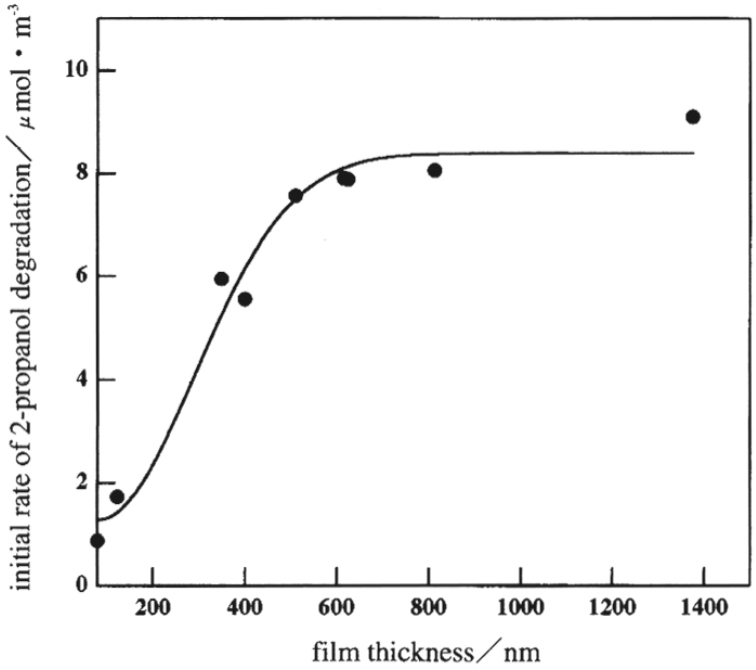


Figure 5. Relationship between initial rate of 2-propanol degradation and the thickness of TiO_2 particulate films. The TiO_2 film was prepared by depositing the TiO_2 particles after 48 h grinding treatment (particle size; 30 nm).

Effect of surface area. The dependence of surface area of the particulate films on film thickness is represented in figure 6. TiO_2 particulate films deposited with 30 nm TiO_2 particles (after 48 h grinding treatment) were used in this experiment. The surface area of the films increased linearly with increasing film thickness, even above 600 nm, at which the photocatalytic activity reached a saturated value. This result suggests that the surface area of the films is not responsible for the saturation of photocatalytic activity at thick films.

Effect of light transmission in the particulate film. In order to examine the transmission of UV light in the particulate films, the effect of light intensity on the photocatalytic activity was studied for thin and thick films. In the case of the thin film, through which most of the irradiated UV light passes, the reaction rate reaches saturated value at a certain light intensity. Meanwhile, if the greater part of the irradiated light is absorbed by the thick film, it is expected that photocatalytic activity continues to increase with increasing UV light intensity, even above the threshold value observed at the thinner film. Figure 7 shows the photocatalytic activity of thin (120 nm) and thick (600 nm) films as a function of irradiated light intensity. The threshold values of light intensity above which the activity saturates were observed for the thick film as well as the thin film and these values were almost the same for both films. These results suggest that the saturation of photocatalytic activity above a certain film thickness was not caused by the retardation of UV light transmission due to absorption.

Effect of recombination of photogenerated electron-hole pairs. Charge separation efficiency of photo-generated holes and electrons is another important index of photocatalytic activity (Kubokawa *et al.* 1988). Near the surface of TiO_2, a space

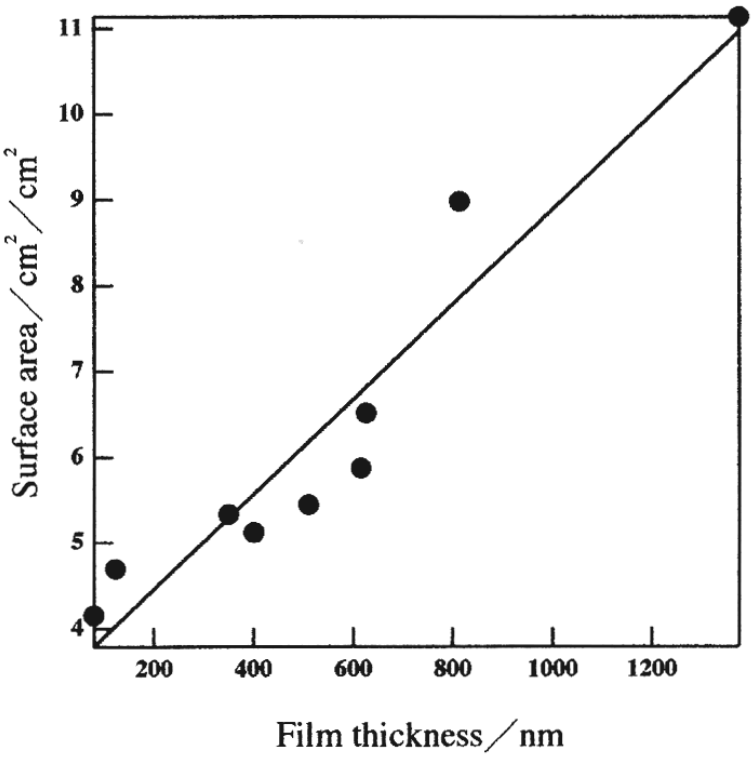


Figure 6. Surface area of TiO_2 particulate films as a function of film thickness. TiO_2 films were prepeared by depositing the TiO_2 particles after 48 h grinding treatment (particle size; 30 nm).

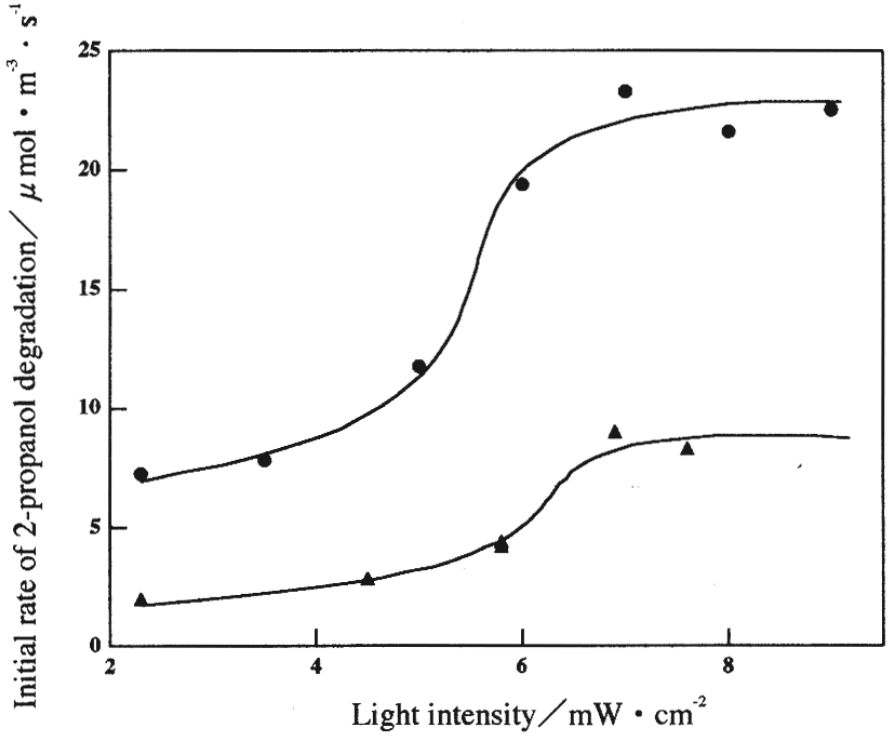
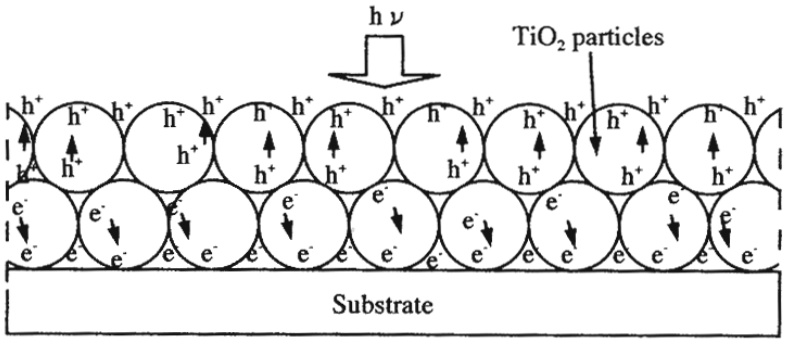
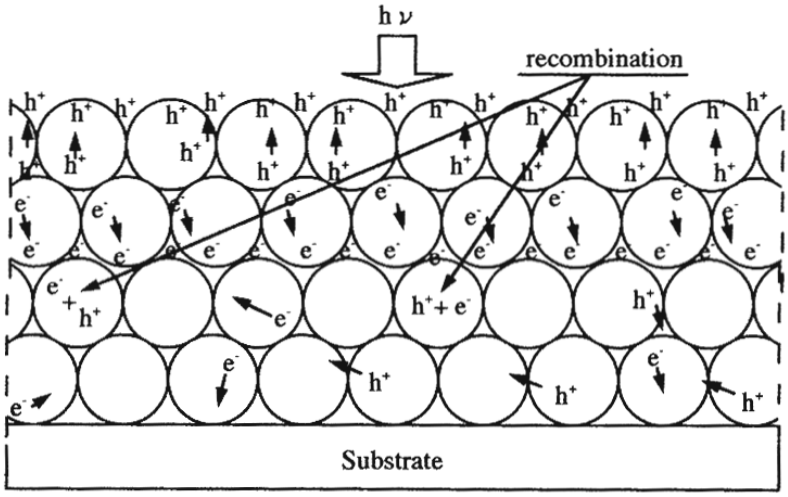


Figure 7. Relationship between initial rate of 2-propanol degradation and the light intensity. The TiO_2 films were prepared by depositing the TiO_2 particles after 48 h grinding treatment (particle size; 30 nm). The thickness of TiO_2 particulate films is ● 800 nm; ▲ 120 nm.



(a) Thin particulate film



(b) Thick particulate film

Figure 8. Model of photoinduced charge separation in the TiO_2 particulate films.

charge layer is formed and this moves photogenerated holes and electrons to the surface and bulk, respectively, preventing them from recombination (figure 8(a)). In the case of thin films, the amount of the photogenerated holes moving to the interface increases with increasing film thickness, resulting in the enhancement of photocatalytic activity. Meanwhile, in the case of thick films, formation of a space charge layer cannot expand to the whole film, and recombination of photogenerated holes and electrons in the bulk film is promoted (figure 8(*b*)). Therefore, the amount of photogenerated holes capable of moving to the surface becomes constant above a certain film thickness, resulting in the saturation of photocatalytic activity.

Effect of length of grinding treatment on photocatalytic activity

In order to examine the effect of grinding treatment, i.e. the size of TiO_2 particles, on the photocatalytic activity, initial rates of 2-propanol degradation on the irradiated TiO_2 particulate films deposited with TiO_2 particles ground for various times were plotted against film thickness (figure 9). In the following, results will be discussed for thin films and thick films, respectively.

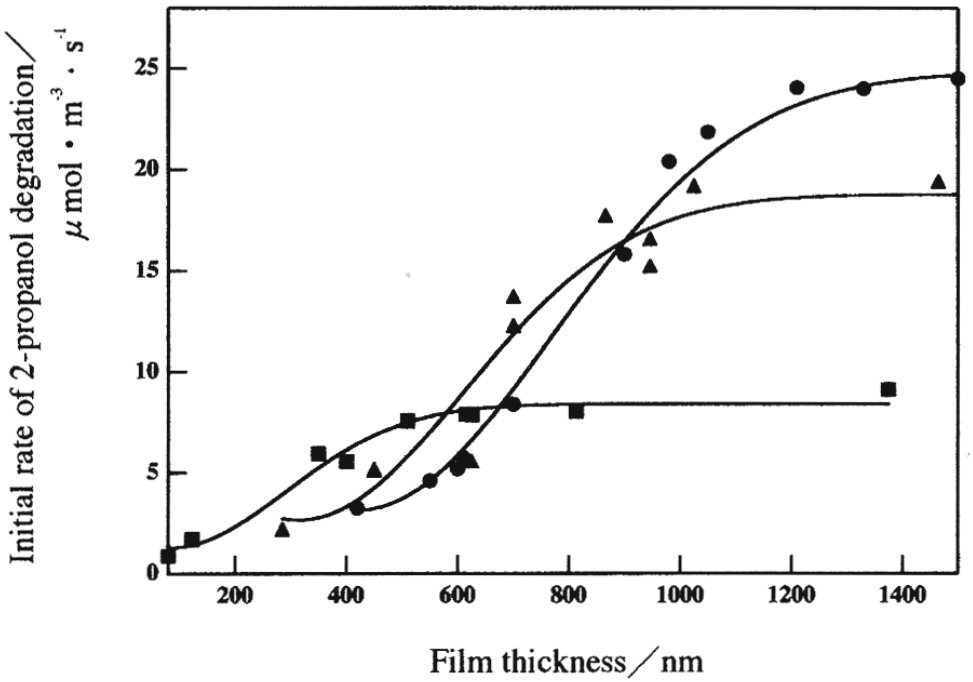


Figure 9. Relationship between initail rate of 2-propanol degradation and the thickness of TiO_2 particulate film. The TiO_2 films were prepared by depositing TiO_2 particles after ▲ 5 h grinding (particle size: 110 nm), ● 15 h grinding (particle size: 70 nm), ■ 48 h grinding (particle size: 30 nm).

Table 1. Relationship between surface area and the deposited particle size in the TiO_2 particulate films.

Grinding time/h (Particle size/nm)	5 (140)	15 (70)	48 (30)
Thickness/nm	400	280	80
Surface area/cm^3/cm^3	2.32	2.79	4.22

Thin films (thickness below 600 nm). For films whose thickness is below 600 nm, the photocatalytic activity was higher when smaller particles (i.e. particles ground for longer times) were deposited onto the substrate, as shown in figure 9. The surface area of the films (number of dipping) loaded with particles of each size (110, 70, 30 nm) was measured by utilizing adsorption of cyanine dye NK-3422 on the film surface. Calculated surface areas of the films are summarized in table 1. These results reveal that the surface area is larger for the films deposited with smaller particles, in spite of the decrease in film thickness measured by cross-sectional observation with SEM.

Thus, the increase in photocatalytic activity for films deposited with smaller particles is due to the increase in the surface area of the particulate films.

Thick films (thickness above 1000 nm). As mentioned earlier, the photocatalytic activity of the particulate films reached a saturated value above a certain film thickness. Furthermore, this saturated value of photocatalytic activity decreased with increasing the length of grinding.

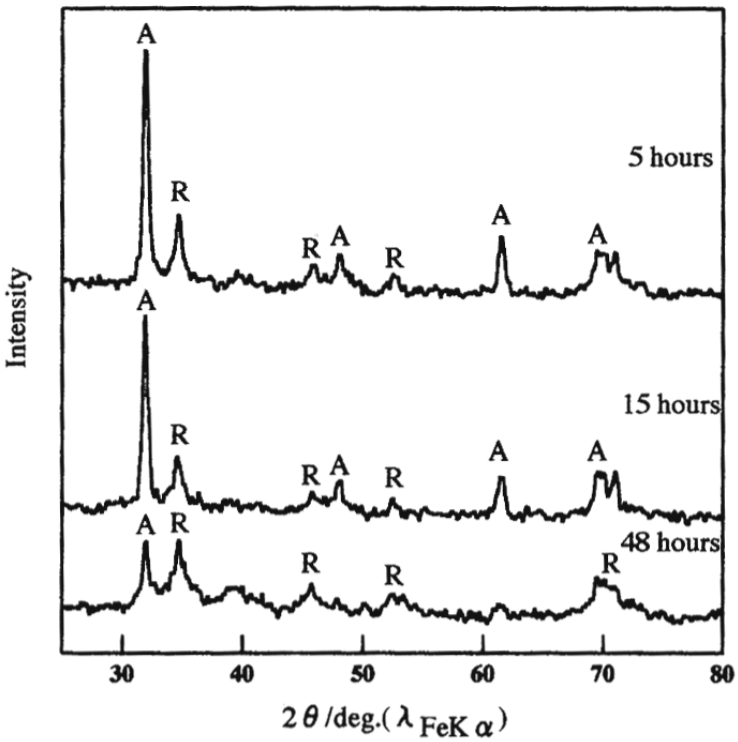


Figure 10. X-ray diffraction patterns of TiO_2 particles as a function of grinding time in cyclohexanon. A: anatase, R: rutile.

X-ray diffraction measurements were done for TiO_2 particles after grinding treatment for various times, and the results are shown in figure 10. Diffraction peaks attributed to anatase were found to decrease with increasing length of grinding treatment in cyclohexanone, while peaks attributed to rutile remained unchanged. Disorder of the crystal lattice in the vicinity of the surface is known to be induced during grinding treatment, and this causes a decrease in the peak strength and broadening of the peak width at the X-ray diffraction measurement (Kubo *et al.* 1963). Anatase structure of P-25 may be also destroyed with grinding treatment in cyclohexanone to form an amorphous structure. Photocatalytic activity of TiO_2 is reported to be affected by its crystal structure and the anatase form generally gives the best catalytic activity (Nishimoto *et al.* 1985, Bickley *et al.* 1991, Cerrábo *et al.* 1993, Ohtani and Nishimoto 1993). Accordingly, a decrease in photocatalytic activity at thick films deposited with particles ground-treated for longer hours is mainly caused by the collapse of anatase crystal to the amorphous forms during the grinding treatment.

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