Effect of Plasma-Polymerized Layer Formed on a Surface of Titanium Dioxide Particle on Its Photocatalytic Activity*

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If TiO₂ particles are used as components of paint without any surface modification, binding resin of the paint will be easily decomposed by the photocatalytic activity of the particles. In this work, plasma polymerization of octamethylcyclotetrasiloxane as a siloxane monomer is tried to form thin layer stable to the photocatalytic activity on the surface of TiO₂ particles. The plasma-polymerized layer containing Si-O and Si-C bonds is formed on the surface of the particles and shows stability to the photocatalytic activity of TiO₂. The particles surface-modified with the plasma polymerization exhibit visible-light activity. The visible-light activity is originated from carbon doping which brings about in the particles during the plasma polymerization, and is thermally stable to be maintained after annealing at 673 K.

1. Introduction

Visible-light-active (vis-active) TiO₂ has been prepared by various methods¹⁻⁹. According to Takeuchi et al.¹ and Ihara et al.², the reduction of TiO₂ by hydrogen plasma treatment with elevated temperatures created a new absorption band in the visible-light region and showed photocatalytic activity in this region.

Vis-active TiO₂ films and powders were prepared by a nitrogen-doping³⁻⁶. According to Asahi et al.³, TiO_{2-x}N_x films were prepared by the sputtering of TiO₂ target in N₂(40%)/Ar gas mixture, and TiO_{2-x}N_x powders were prepared by the treatment of anatase TiO₂ powders in NH₃(67%)/Ar atmosphere at 873 K for 3 h. Nitrogen-doped TiO₂ powders were also prepared by the oxidative annealing of TiN powders for 90 min in an oxygen gas flow at 823 K⁴. According to Irie et al.⁵, TiO_{2-x}N_x powders were prepared by the annealing of anatase TiO₂ powders under NH₃ flow at 823, 848, and 873 K for 3 h. Nitrogen-doped TiO₂ particles were also prepared by a series of argon and nitrogen plasma treatment⁶. The TiO₂ particles having Ti-N bonds formed by substitutional nitrogen-doping showed photocatalytic activities under visible-light irradiation (vis irradiation).

Sulfur-doped TiO₂ powders into which the oxidation state of the S atoms is incorporated showed visible light activity (vis activity)⁷. Carbon-doped TiO₂ powders showing vis activity were fabricated by oxidative annealing of TiC, in which the doped carbons were located at oxygen sites⁸. Carbonate-species-doped TiO₂ showed also vis activity⁹.

For the improvement of the thermal stability of the photocatalytic activity in TiO₂ powders, silica-modified

TiO₂ powders were prepared by the glycothermal method¹⁰. In the silica-modified TiO₂ powders, the presence of Si in the TiO₂ lattice seems to contribute to the deceleration of the grain growth of anatase and the suppression of anatase-rutile transformation. The silica-modified TiO₂ powders after nitrogen doping by a treatment at 873 K with NH₃ exhibited a high photocatalytic activity under vis irradiation¹¹.

If TiO₂ particles are used as fillers in the paint, binding resin of the paint will be decomposed by photocatalytic activity of the particles under UV irradiation. In this work, a thin layer that is stable to the photocatalytic activity is tried to be formed on the surface of TiO₂ particles by plasma polymerization of a siloxane monomer to depress the decomposition of the binding resin. Since the inherent photocatalytic activity of the particles will be decreased by the formation of the plasma-polymerized layer, the layer should be optimized to depress both the decomposition of the binding resin and the decrease in the photocatalytic activity. Relationship between structure of the thin layer and photocatalytic properties in TiO₂ particles is investigated in this work. Furthermore, possibilities of plasma doping with constituent atoms of the siloxane monomer and an emergence of vis activity are also investigated for the plasma-polymerized TiO₂ particles before and after annealing.

2. Experimental

2.1 Plasma polymerization

Anatase-type TiO₂ particles (ST01, Ishihara Sangyo Co., Osaka, Japan) were used in this work. The average diameter of the primary particles is about 7 nm. A round-bottomed flask-type reactor was used for the treatment of the particles with inductively coupled plasma at 13.56 MHz. The particles introduced into the reactor were evacuated for 1 day with a vacuum system and then were pretreated with argon plasma at 100 W at argon pressure of 13 Pa for 60 min. The reactor was rotat-

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ed at 32 rpm during the plasma treatment for homogeneous treatment of the particles. Then the particles were plasma-polymerized with octamethylcyclotetrasiloxane as a monomer. The discharge power was 30 W, the discharge time was in the range of 10 to 50 min, and the monomer pressure was 11 Pa. The reactor was also rotated at 32 rpm during the plasma polymerization.

2.2 Surface analyses of plasma-polymerized TiO₂ particles

For the confirmation of the formation of the plasma-polymerized layer on the surface of the TiO₂ particles, surface area and pore distribution of the particles were measured before and after plasma polymerization with Thermo Quest Sorptmatic 1990 (Thermo Quest Co., Italy). The TiO₂ particles had been heated at 423 K for 10 h to remove water molecules adsorbed on the surface of the particles before the measurement.

An infrared spectrum of the surface of the plasma-polymerized TiO₂ particles was measured with Magna 550 Fourier transform infrared spectroscopy (Nicolet Analytical Instruments, Madison, WI) equipped with Barnes analytical diffuse reflectance accessory to identify the chemical structure of the plasma-polymerized layer. X-ray photoelectron spectroscopy (XPS) measurement was carried out with Shimadzu ESCA750 X-ray photoelectron spectroscopy (Shimadzu Co., Kyoto, Japan) to clarify a change in the surface structure of the TiO₂ particles after the plasma polymerization. The infrared spectroscopy and XPS measurements were also carried out to clarify the effect of the irradiation of a 150 W Xe lamp on the surface state of the plasma-polymerized TiO₂ particles.

X-ray diffraction (XRD) intensity curves of the particles before and after the plasma polymerization were measured with Rigaku Rint 1200 X-ray diffractometer (Rigaku Denki Co., Tokyo, Japan) to clarify the crystal structure of the TiO₂ particles after the plasma polymerization.

2.3 Thermal stability of plasma-polymerized TiO₂ particles

The thermal degradation behavior of the plasma-polymerized TiO₂ particles was measured at a heating rate of 5 Kmin⁻¹ at a dry air-flow rate of 10 mLmin⁻¹ with a TG/DTA200 system (Seiko Denshikogyo Co., Chiba, Japan). The weight of the sample was 10 mg. The plasma-polymerized TiO₂ particles were annealed in air at 673 K for 60 min and a change in the surface structure of the particles with annealing was analyzed with infrared spectroscopy and XPS.

2.4 Photocatalytic properties of plasma-polymerized TiO₂ particles

UV-vis diffuse reflectance spectra of the plasma-polymerized TiO₂ particles were measured with JASCO V-500 UV-vis spectrophotometer (JASCO International Co., Tokyo, Japan) equipped with integral-sphere attachment to clarify a change in light absorbance behavior after the plasma polymerization. The plasma-polymerized particles were immersed into 1 mM methylene blue of water solution for 1 day in the dark to adsorb methylene blue molecules. The particles were

washed with pure water and then dried in vacuo at 303 K for 1 h.

A 150 W Xe lamp as the light source and two cutoff filters for UV region (wavelength < 420 nm) and IR region (wavelength > 750 nm) were used to obtain the visible light. Methylene blue adsorbed on the surface of the TiO₂ particles was irradiated with the visible light for 3 h. A decrease in absorbance at 664 nm of methylene blue was measured for the evaluation of the photocatalytic properties of plasma-polymerized TiO₂ particles.

3. Results and Discussion

3.1 Surface analyses of plasma-polymerized TiO₂

Figure 1 shows pore distributions of TiO₂ particles before and after plasma polymerization. The maximum distribution was around 1.5 nm before the plasma polymerization, whereas a slight broadening to the smaller pore size took place after the plasma polymerization. The pores could be formed among the primary particles or the secondary ones which are aggregated one another. Specific surface areas before and after the plasma polymerization were 322.6 and 245.3 m²g⁻¹, respectively. These results mean that the pore size is decreased by the plasma-polymerized layer formed on the surface of the aggregated particles in the pores.

Figure 2 shows infrared spectra of the surface of TiO₂ particles before and after plasma polymerization. There are several absorption bands newly observed after the plasma polymerization. Absorption bands around 1120 and 1270 cm⁻¹ are assigned to C-O stretching of ester group, while those around 775 and 1250 cm⁻¹ to Si-CH₃

Fig. 1 Pore distributions of TiO₂ particles (a) before and (b) after plasma polymerization. Plasma polymerization time, 20 min.

stretching and that around 1650 cm^{-1} to $\text{C}=\text{O}$ stretching of ester group. Therefore it becomes apparent that the plasma-polymerized layer is composed of fragments that are not necessarily originated from the monomer.

Figure 3 shows Si/Ti atomic ratio at the surface of the plasma-polymerized TiO_2 particles as a function of plasma polymerization time. The atomic ratio is evaluated by using XPS peak-strength ratio, $\text{Si}_{2p}/\text{Ti}_{2p}$. The ratio was increased with increasing polymerization time up to around 35 min and then was decreased. On the other hand, C/Ti atomic ratio was little changed in the range of plasma polymerization time. The plasma polymerization would preferentially take place up to around 35 min, whereas abrasion or peeling off of the plasma-polymerized layer would preferentially take place after that. The Gibbs free energy of an addition polymerization contains enthalpy and entropy terms, that is, $\Delta G = \Delta H - T\Delta S$. When the reaction temperature is raised above the ceiling temperature of the polymerization, T_c , polymer formation cannot proceed spontaneously¹²⁾. The ceiling temperature of polymerization in gas phase would be much lower than that in the liquid phase. Since the plasma polymerization is exothermic, the temperature of TiO_2 particles will be raised with increasing plasma polymerization time. It can therefore be presumed that the temperature of TiO_2 particles goes up to over the T_c at plasma polymerization time of around 35 min.

Figure 4 shows weight reduction of plasma-polymer-

Fig. 2 Infrared spectra of the surface of TiO_2 particles before and after plasma polymerization. Plasma polymerization time, 30 min.

Fig. 3 Si/Ti atomic ratio on the surface of the plasma-polymerized TiO_2 particles as a function of plasma polymerization time.

ized TiO_2 particles as a function of plasma polymerization time. The weight reduction was measured in the temperature range of 473 to 1273 K to eliminate low molecular weight molecules such as the monomer adsorbed on the plasma-polymerized layer of the particles. The weight reduction of the particles before the plasma polymerization was 3.9%, since contaminants and water molecules had been adsorbed on the surface. The weight reduction was increased with increasing polymerization time up to around 35 min and then was decreased, which coincides with Si/Ti ratio shown in Figure 3. Si/Ti ratio was in the range of 0.2 to 0.24 after the heating. This fact means that thermally stable Si-containing layer is formed on the surface after the heating.

3.2 Stability of plasma-polymerized layer for TiO_2 photocatalytic activity

Figure 5 shows Si/Ti, C/Ti, and O/Ti atomic ratios in plasma-polymerized TiO_2 particles as a function of irradiation time with the Xe lamp. The Si/Ti and C/Ti ratios were decreased with increasing irradiation time up to 4 h and then were almost kept constant. The O/Ti ratio was decreased in a similar manner as Si/Ti and C/Ti and then was kept at around 3.3. Therefore it becomes apparent that the plasma polymerized layer stable to the photocatalytic activity of the particles is considerably remained after the irradiation. **Figure 6** shows infrared spectra of the surface of plasma-polymerized TiO_2 particles before and after the irradiation of the Xe lamp. The absorptions for Si-CH₃ stretching (775 and 1250 cm^{-1}), C-O stretching of ester group (1120 and 1270 cm^{-1}), and Si-O-Si and Si-O-C skeletal vibrations (1020 – 1090 cm^{-1}) were distinctly decreased after the irradiation, whereas the broad absorptions for Si-C and Si-O stretchings (870 – 900 cm^{-1}) were increased. It is assumed from Figures 5 and 6 that silica- and silicon carbide-like structure mainly composed of Si-O and Si-C bonds is remained after the irradiation, since the great decrease in absorbance of the functional groups and the broadening of the spectrum take place and Si, C, and O atoms are considerably contained in the plasma-polymerized layer after the irradiation.

3.3 Photocatalytic properties of plasma-polymerized TiO_2 particles

Figure 7 shows absorbance reduction at 664 nm of methylene-blue-adsorbed TiO_2 particles after vis irradiation.

Fig. 4 Weight reduction of plasma-polymerized TiO_2 particles as a function of plasma polymerization time.

tion as a function of plasma polymerization time. A decrease in the absorbance after vis irradiation is divided by the absorbance before the irradiation to evaluate the absorbance reduction in Figure 7. The reduction tended to increase with increasing polymerization time up to around 35 min, and then decreased. Therefore, it becomes apparent that the particles having the plasma-

Fig. 5 (a) Si/Ti, (b) C/Ti, and (c) O/Ti atomic ratios of plasma-polymerized TiO_2 particles as a function of irradiation time with 150 W Xe lamp. Plasma polymerization time, 20 min.

Fig. 6 Infrared spectra of the surface of plasma-polymerized TiO_2 particles before and after irradiation of 150 W Xe lamp. Plasma polymerization time, 30 min; irradiation time, 6 h.

polymerized layer show vis activity. **Figure 8** shows UV-vis diffuse reflectance spectra of TiO_2 particles before and after the plasma polymerization. The particles surface-modified with the plasma polymerization revealed visible light absorption.

A peak assigned to Ti-C bonds was observed nearby at 281.8 eV in C_{1s} XPS spectrum of carbon-doped TiO_2 powders⁸⁾. In carbonated species-doped TiO_2 powders, C_{1s} peaks at 284 and 288 eV were observed after calcinations at 673 and 773 K⁹⁾. The peak around 284 eV was assigned to carbon adsorbed on the surface of TiO_2 as a contaminant (contamination of organic residues on the surface). The latter peak around 288 eV suggests the presence of a carbonate species. **Figure 9** shows C_{1s} XPS spectra of TiO_2 particles before and after the plasma polymerization. C_{1s} peak for a contaminant appeared around 284.5 eV before the plasma polymerization. C_{1s} peak around 282 eV appeared after the plasma polymerization. Therefore it becomes apparent that Ti-C bonds are formed in the surface area of the particles by the plasma polymerization and carbon doping inducing the formation of Ti-C bonds brings about the vis activity. It is assumed that silicon doping during the plasma polymerization is difficult, compared with the carbon doping, since the size of Si atoms is much larger than that of C atom. A shoulder around 286 eV is assigned to C-O bonds. According to Asahi et al.³⁾, carbon doping

Fig. 7 Absorbance reduction of methylene-blue-adsorbed TiO_2 particles as a function of plasma polymerization time.

Fig. 8 UV-vis diffuse reflectance spectra of TiO_2 particles before and after plasma polymerization. Plasma polymerization time, 30 min.

produces states in the band gap of TiO_2 that absorb visible light. If the states in the gap are overlapped sufficiently with the band states of TiO_2 , photoexcited carriers, that is, holes and electrons will be transferred to reactive sites at the catalyst surface within their lifetime. Since the carbon-doped TiO_2 prepared by the plasma polymerization shows the vis activity, the states due to carbon doping would be overlapped with the valence band state.

It may be originated from decrease in amount of doped carbon that the absorbance reduction of decomposition of methylene blue molecules was decreased above the plasma-polymerization time of around 35 min, as shown in Figure 7. **Figure 10** shows $\text{C}(\text{Ti-C})/\text{Ti}$ atomic ratio as a function of plasma polymerization time. Since the amount of $\text{C}(\text{Ti-C})/\text{Ti}$ in the plasma

polymerized particles is very large, in the range of 0.62 to 0.74, it is assumed that the formation of Ti-C bonds does not necessarily mean carbon doping into the particles. The significant amount of Ti-C bonds is formed in the interface region of the plasma-polymerized layer and TiO_2 particles, but the certain extent of carbon doping in the particles is realized to show the vis activity. It becomes apparent from XRD patterns of plasma-polymerized particles that anatase phase remained without collapse and the formation of another crystalline phase was not detected. Therefore it is supported that the certain extent of carbon doping is realized for the vis activity. The amount of $\text{C}(\text{Ti-C})/\text{Ti}$ was increased with increasing plasma polymerization time up to around 30 min and then was decreased. If the amount of $\text{C}(\text{Ti-C})$ varies in proportion to that of the carbon doping associated with the vis activity, the decrease in the absorbance reduction above 35 min would be mainly originated from the decrease in $\text{C}(\text{Ti-C})/\text{Ti}$.

3.4 Effect of annealing on photocatalytic property of plasma-polymerized TiO_2 particles

Plasma-polymerized (30 min) TiO_2 particles were annealed in air at 673 K for 60 min. For XPS measurement, all atomic ratios against Ti, that is, Si/Ti , C/Ti , O/Ti , and $\text{C}(\text{Ti-C})/\text{Ti}$ ratios, decreased 12–16% after the annealing. **Figure 11** shows infrared spectra of the surface of the plasma-polymerized TiO_2 particles before and after the annealing. The absorptions for Si-CH_3 stretching (775 and 1250 cm^{-1}) almost disappeared and the broad absorption ($1020\text{--}1090\text{ cm}^{-1}$) for Si-O-Si and Si-O-C skeletal vibrations largely decreased, whereas a broad peak which would be recognized in silica- and silicon carbide-like structure appeared in the range of 700 to 900 cm^{-1} .

In the absorbance measurement of methylene-blue-adsorbed TiO_2 particles after plasma polymerization, the absorbance reduction after annealing was diminished to 46% of that of before annealing and the vis activity was remained. It will be attributable to a change in the structure of the plasma-polymerized layer with annealing, as shown in Figure 11, that the decrease in the absorbance reduction became larger compared to that in $\text{C}(\text{Ti-C})/\text{Ti}$. Therefore the decrease in the vis activity af-

Fig. 9 C_{1s} XPS spectra of TiO_2 particles (a) before and (b) after plasma polymerization. Plasma polymerization time, 30 min.

Fig. 10 $\text{C}(\text{Ti-C})/\text{Ti}$ atomic ratio as a function of plasma polymerization time. $\text{C}(\text{Ti-C})$ shows the amount of carbons in Ti-C bonds.

Fig. 11 Infrared spectra of the surface of plasma-polymerized TiO_2 particles before and after annealing in air at 673 K for 60 min. Plasma polymerization time, 30 min.

ter the annealing would be originated from the decrease in the amount of carbon doping and the formation of dense structure in the plasma-polymerized layer after the annealing.

4. Conclusion

Plasma-polymerized thin layer of octamethylcyclotetrasiloxane on TiO_2 particles has silica- and silicon-carbide-like structure which is stable to the photocatalytic activity of the particles. The plasma-polymerized TiO_2 particles exhibit vis activity. The carbon doping which is confirmed by the appearance of C_{1s} peak around 282 eV in the plasma-polymerized particles is realized with the plasma polymerization. The amount of carbon doping and the vis activity are decreased by annealing at 673 K, but are maintained to a certain extent.

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