

ARTICLES

Size Control of Titanium Oxide Sheets by Regulating Catalysis in a Catalytic Sol–Gel Process and Their UV Absorption Properties

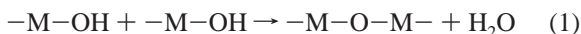
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Catalysis in a sol–gel process of titanium alkoxide was switched off to control the size of sheetlike particles of a resulting titanium oxide. The oxide growth was suspended by adding acetic acid, which regulated the catalytic activity of ammonium acetate. An ultraviolet–visible absorption band depended on the size of sheetlike particles. A lower energy region appeared for the larger size ($> 1 \mu\text{m}$) of sheetlike particles but not for the smaller one. It is probably due to a bridging bidentate of acetate on the flat surface of titanium oxide particles.

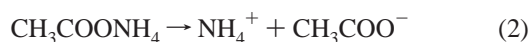
Introduction

The sol–gel process of converting titanium alkoxides to titanium oxide polymer has been widely studied as a preparation method for ultrafine particles^{1–3} and monolithic gels^{4,5} of titanium dioxide under mild conditions. We have found that a salt catalyst such as ammonium carbonate or ammonium acetate accelerated reactions in a sol–gel process more effectively than conventional catalysts such as acid catalysts (e.g. HCl, HNO₃ or CH₃COOH), or base catalysts (e.g. aqueous ammonia).^{6,7} The sol–gel process consists of hydrolysis of titanium alkoxides and the subsequent polycondensation. The dehydrative polycondensation of two M–OH species consists of deprotonation of one hydroxy species and dehydroxylation of the other to form M–O–M oxo species and water:

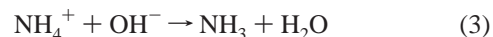


In organic chemistry, a base catalyst accelerates the deprotonation while an acid catalyst accelerates the dehydroxylation. An acid–base pair catalyst is expected to accelerate the overall polycondensation.

If a strong acid and a strong base are mixed, they neutralize each other and the resulting salt does not act as an acid–base pair catalyst. However, the salt neutralized from a weak acid and a weak base is expected to act as an acid–base pair catalyst: an anion acts as a base while a cation acts as an acid. For example, ammonium acetate decomposes to an ammonium ion and an acetate ion in the solution:



The ammonium ion reacts with a hydroxy ion to form ammonia and water:



which is the reverse reaction of a base dissociation. Reaction 3 proceeds because ammonia is a weak base, while an ammonium ion acts as an acid catalyst. The acetate ion accepts a proton to form acetic acid:



which is the reverse reaction of an acid dissociation. Reaction 4 proceeds because acetic acid is a weak acid, while an acetate ion acts as a base catalyst.

In a sol–gel process, to obtain a monolithic gel, branching of a metal oxide growth is actively restricted. In the branching of the metal oxide, a spherical particle was formed and precipitated. In order to polymerize without branching, hydrolysis was reduced to decrease the number of hydroxy groups. These are reactive sites for polycondensation. In the case of a sol–gel process of titanium alkoxide, polycondensation is naturally slow. The polycondensation rate decreased according to the number of hydroxy groups. There was almost no polycondensation in the restricted conditions. It is not until we found catalysis in a sol–gel process that the monolithic gel of a titanium oxide was synthesized under control. It is necessary to develop the techniques of catalysis of sol–gel processes for a new field of physical chemistry.

In this study, we switched off the catalysis for polycondensation of the sol–gel process of titanium alkoxide to control the particle size of the resulting titanium oxide. If the catalysis was deactivated after particles of titanium oxides were grown up to an appropriate size, their sizes were controlled. We used ammonium acetate as a catalyst to obtain a titanium oxide gel. Acetate ion is a base catalyst which accepts a proton, as in reaction 4. However, when acetic acid was added, reaction 4 became slow, stopped, or proceeded in reverse. We succeeded in controlling the size of the sheetlike titanium oxide and measured the resulting particles.

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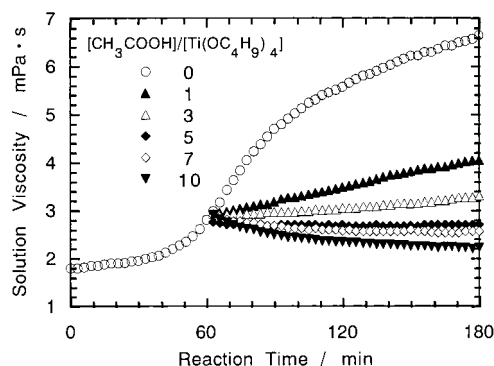


Figure 1. Time course of viscosity of the solution containing $[\text{Ti}(\text{C}_4\text{H}_9)_4] = 0.05 \text{ M}$, $[\text{CH}_3\text{COONH}_4] = 0.05 \text{ M}$, and $[\text{H}_2\text{O}] = 0.5 \text{ M}$. Various amounts of acetic acid were added after the reaction for 60 min.

Experimental Section

All water used in this study was deionized by Aquarius GS-200 System (Advantech). Titanium tetra-*n*-butoxide (Kanto Chemical Co., Inc., >97%), ammonium acetate (Kanto Chemical Co., Inc., special grade reagent), acetic acid (Wako Pure Chemical Industries, Ltd., super special grade reagent), and 1-butanol (Wako Pure Chemical Industries, Ltd., special grade reagent). These were used without further purification.

In nitrogen atmosphere, 10 mL of butanol solution containing 1.25 mmol of tetra-*n*-butoxide, and 15 mL of another butanol solution containing 1.25 mmol of ammonium acetate as a salt catalyst, and 12.5 mmol of water were prepared. A sol-gel reaction started when the two butanol solutions were mixed to be a total of 25 mL (0.05 M tetra-*n*-butoxide, 0.5 M H_2O , and 0.05 M ammonium acetate). Reaction temperature was kept constant at 25 °C with a circulated water bath. The reaction process was followed by measuring solution viscosity (Yamaichi Electronic, Viscomate VM-1A-L). At different fixed intervals after the sol-gel reaction started, 5 mL of the butanol solution of acetic acid was added. In order to stop the particle growth, 8.75 mmol of acetic acid (seven times as large as titanium alkoxide) was used.

Ultraviolet-visible (UV-vis) absorption spectra of sols were obtained using a spectrometer (Shimadzu UV-2400PC). Sols were dispersed with methanol and dropped on smooth plates of a cleaved, highly oriented pyrolytic graphite, dried under vacuum for 4 h and observed in morphology with a high-resolution scanning electron microscope (HR-SEM, JEOL JMS-6100F). They were also washed with methanol, dried at 90 °C in air, and ground to powder. Dried particles were measured by a thermal gravimetry-differential thermal analysis (TG-DTA, Rigaku TAS-200). They were heated at a rate of 3 °C min^{-1} , held at 200 °C for 30 min, and heated again to 800 °C. Sample for X-ray diffraction (XRD, Rigaku CN-2028) and infrared absorption spectra was pretreated according to the temperature program of TG-DTA. After reaching certain temperatures, the powders were cooled. Infrared absorption spectra of the sample powders diluted with KBr were obtained with a spectrometer (Perkin-Elmer 1650FTIR) by the transmission method.

Results and Discussion

Control of Catalysis in a Catalytic Sol-Gel Process. When ammonium acetate was added as a catalyst, the solution viscosity increased slowly with reaction time as shown in Figure 1. After 60 min, it rose rapidly and increased gently again after 90 min. When acetic acid was added to the solution at 60 min, the viscosity curve changed. The viscosity increase declined with

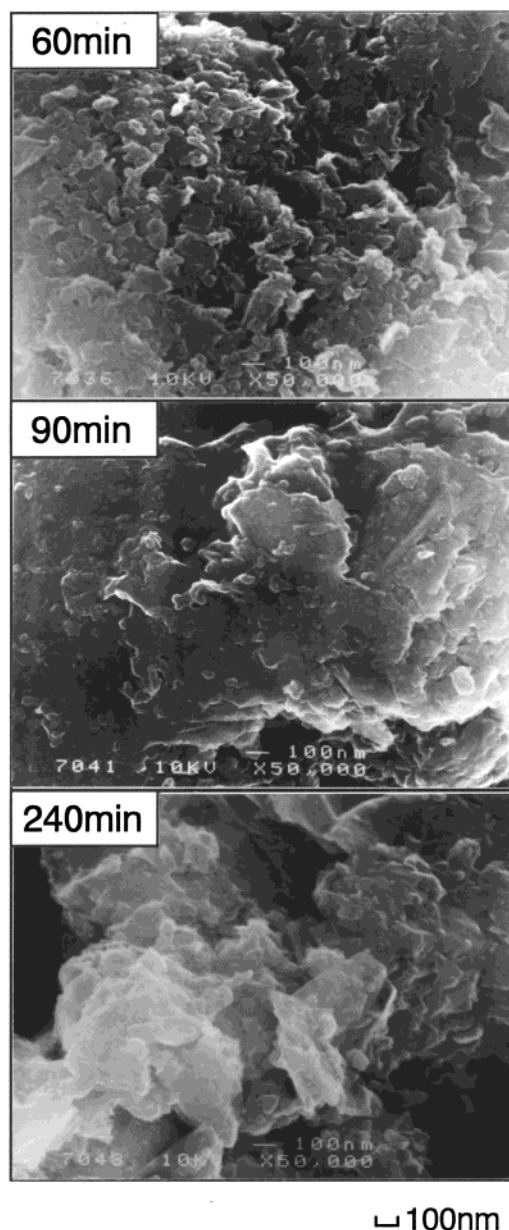


Figure 2. High-resolution scanning electron micrographs of titanium oxide grown with acetic acid in a catalytic sol-gel process using ammonium acetate ($[\text{Ti}(\text{C}_4\text{H}_9)_4] = 0.05 \text{ M}$, $[\text{CH}_3\text{COONH}_4] = 0.05 \text{ M}$, and $[\text{H}_2\text{O}] = 0.5 \text{ M}$). Acetic acid (8.75 mmol) was added at 60, 90, and 240 min.

an increase in the amount of acetic acid added. When the acetic acid added was 5–7 times as large as titanium alkoxide, the viscosity increase almost stopped. A larger amount of acetic acid added resulted in the decrease in viscosity. In the following experiments, 8.75 mmol of acetic acid (seven times as large as titanium alkoxide) was used for size control to stop the particle growth.

Figure 2 shows high-resolution scanning electron micrographs of size-controlled particles of titanium oxide. Sheetlike structures were observed for all sols in this experiment. The sheet structure of titanium oxide after 60 min was a few hundred nanometers wide. The sheet was so thick that we looked through a sheet at another sheet. When the reaction was prolonged to 90 min, the lateral size of the sheet structure increased to a few micrometers. The increase in the lateral size corresponds to the rapid rise in viscosity. During further reaction from 90 to 240 min, thin sheets

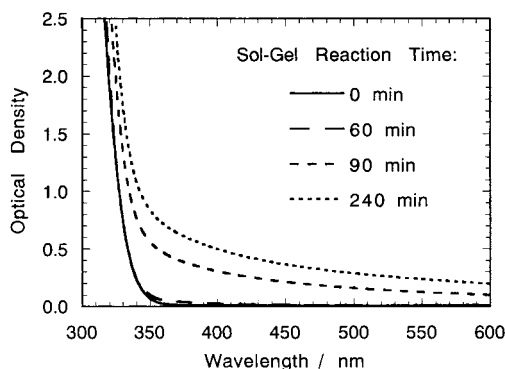


Figure 3. UV-visible adsorption spectra of titanium oxide sols grown with acetic acid in a catalytic sol-gel process using ammonium acetate ($[\text{Ti}(\text{C}_4\text{H}_9)_4] = 0.05 \text{ M}$, $[\text{CH}_3\text{COONH}_4] = 0.05 \text{ M}$, and $[\text{H}_2\text{O}] = 0.5 \text{ M}$). Acetic acid (8.75 mmol) was added at 0, 60, 90, and 240 min.

were stacked without any change in the lateral size, corresponding to the gentle increase in viscosity followed by the rapid rise.

UV Absorption of Size-Controlled Sheets of Titanium Oxide. UV-visible spectra of sols of titanium oxide are shown in Figure 3. Absorption bands were observed below 360 nm for a solution of titanium alkoxide (reaction time is 0 min). The spectrum of the sol after 60 min in reactant was almost the same as that of a solution of titanium alkoxide. However, for another sol after 90 or 240 min, the absorption edge was shifted to longer wavelengths (ca. 340 nm) and a new broad absorption was observed in a wide range of 350–600 nm. We have previously found that a new absorption band around 450 nm was characteristic of a sheet structure of titanium oxide which was prepared by a catalytic sol-gel process with ammonium acetate.⁶ Kamato⁸ and Holding et al.⁹ proposed that the appearance of a new absorption band resulted from surface complexation of titanium oxide with surface modifiers. We concluded that the new absorption band of the sheet structure of titanium oxide was due to surface complexation with adsorbed acetate species which change the band gap of a titanium oxide surface. This experimental data suggests that only the larger size ($> 1 \mu\text{m}$) of the sheet structure has the new absorption band. An adsorbed form of acetate would change with the lateral size of sheet structures.

Adsorption States of Acetate on Size-Controlled Sheet Structures of Titanium Oxide. Figure 4 shows TG-DTA curves of dried powders of titanium oxide grown after 60, 90, and 240 min in reaction with a catalytic sol-gel process using ammonium acetate. For the sample prepared from the reaction for 60 min, three exothermic peaks were observed at 246, 334, and 400 °C while in the case of 90 or 240 min, four exothermic peaks were observed at 250, 321, 389, and 519 °C. Figure 5 shows X-ray diffraction patterns of the dried powders of titanium oxide grown after 60 and 240 min. An anatase structure of titanium oxide appeared at 442 °C while no crystal phase was observed at 374 °C. XRD data (Figure 5) suggests that the DTA peaks at 400 and 389 °C were due to crystallization into anatase. The other peaks were due to desorption of acetate or hydroxy group from titanium oxide. The exothermic peak at 519 °C occurred at 240 min while no peak was observed above the crystallization temperature at 60 min. This difference suggested that the larger size of titanium oxide had strongly coordinated forms of acetates or their decomposed carbon species.

Infrared spectra of dried powders grown in the reaction for 60 and 240 min are shown in Figure 6. A couple of peaks were observed at 1411 (or 1410) and 1528 (or 1534) cm^{-1} for both

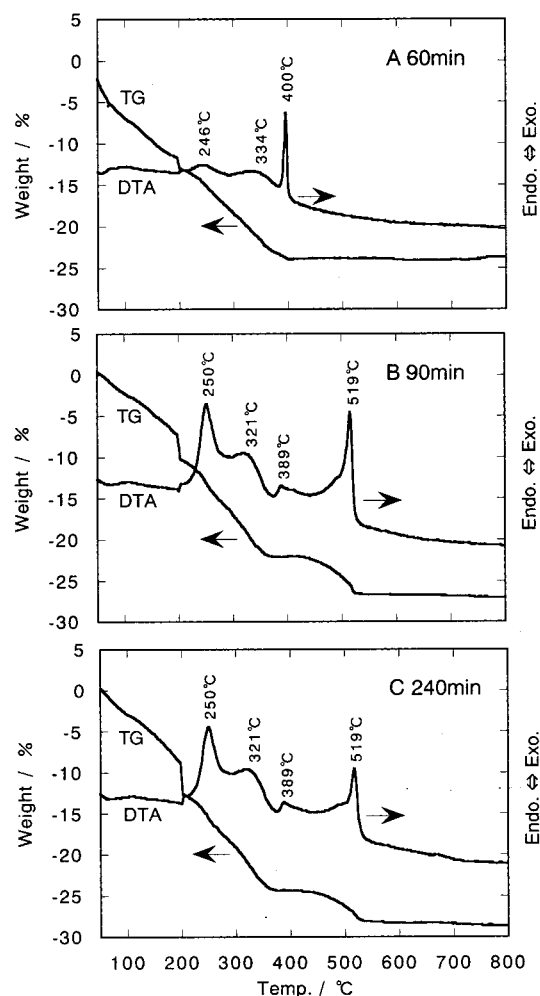


Figure 4. TG-DTA curves of dried powders of titanium oxide grown with acetic acid in a catalytic sol-gel process using ammonium acetate ($[\text{Ti}(\text{C}_4\text{H}_9)_4] = 0.05 \text{ M}$, $[\text{CH}_3\text{COONH}_4] = 0.05 \text{ M}$, and $[\text{H}_2\text{O}] = 0.5 \text{ M}$). Acetic acid (8.75 mmol) was added at (A) 60, (B) 90, and (C) 240 min.

powders. These were found to be due to COO stretching bands of a bidentate of acetate on titanium in previous research.¹⁰ When the particles were heated, the couple of peaks decreased above 207 °C, mostly disappeared at 374 °C, and completely disappeared at 442 °C.

Another couple of peaks were observed at 1346 and 1622 cm^{-1} only for the smaller size of particles at 60 min. The gap between wavenumbers due to symmetric and antisymmetric stretching is 276 cm^{-1} . This gap is much wider than that due to the bidentate (117–124 cm^{-1}), suggesting that the couple of peaks were due to COO stretching bands of a monodentate of acetate.¹⁰ These peaks decreased above 293 °C but remained even at 442 °C. They disappeared completely at 800 °C.

A third couple of broad peaks possibly due to the third state of acetate were observed at 1358 and 1502 cm^{-1} only for large size particles. The gap between wavenumbers due to symmetric and antisymmetric stretching is 144 cm^{-1} . This gap is wider than that in the case of the bidentate, but narrower than that in the case of the monodentate, suggesting that the third couple of peaks was due to COO stretching bands of another bidentate of acetate.¹⁰ There are two bidentate of acetate: a chelating bidentate and a bridging bidentate. The bridging bidentate has a wider gap than the chelating bidentate. The first couple of peaks was due to the chelating bidentate of acetate while the third couple of peaks was due to a bridging bidentate of acetate.

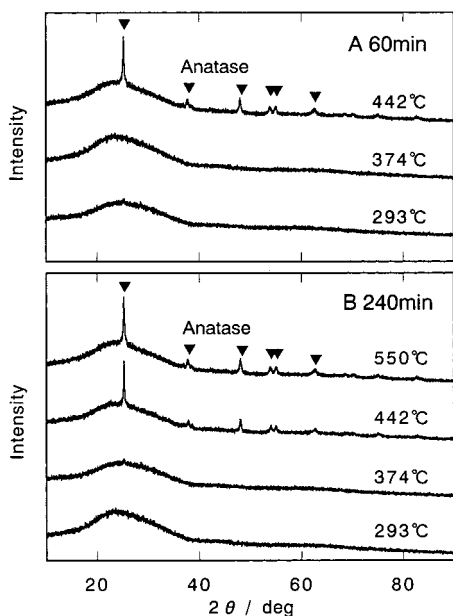


Figure 5. XRD profiles of dried and heated powders of titanium oxide grown with acetic acid in a catalytic sol-gel process using ammonium acetate ($[\text{Ti}(\text{C}_4\text{H}_9)_4] = 0.05 \text{ M}$, $[\text{CH}_3\text{COONH}_4] = 0.05 \text{ M}$, and $[\text{H}_2\text{O}] = 0.5 \text{ M}$). Acetic acid (8.75 mmol) was added at (A) 60 and (B) 240 min. Powders were heated to 293, 374, 442, and 550 °C.

These peaks decreased above 293 °C but remained even at 550 °C, and disappeared completely at 800 °C. This change in infrared spectra suggests that the weight decrease above 400

°C was due to the desorption of this bridging bidentate or its decomposed species. The sample color changed from white into black on heating above 300 °C and turned back into white after the weight decrease at 519 °C. Thermoanalytical data suggests that the bridging bidentate species is coordinated to titanium oxide more strongly than the chelating bidentate and the monodentate. The characteristic UV absorption band is due to the bridging bidentate. The change in the sample color suggests that the bridging bidentate species would be gradually decomposed to the carbon species on heating at 300–500 °C and burned out at 519 °C.

A broad absorption peak was also observed at 3100–3400 cm^{-1} . This peak was due to H-bonded OH vibration of alcohol and H_2O .¹¹ The peak for the smaller size of particles decreased above 293 °C while that for the larger size disappeared at 293 °C. An absorption peak due to the presence of methanol was observed at 1030 cm^{-1} and also disappeared at 293 °C for the large size of particles. The experimental data for the larger size of particles suggests that the peak at 3100–3400 cm^{-1} was due to the presence of methanol. On the other hand, a peak observed at 1030 cm^{-1} mostly disappeared at 207 °C for a small size. Nevertheless, the peak at 3100–3400 cm^{-1} remained at 293 °C and decreased at 374 °C, suggesting the presence of a hydroxy group on the larger size of particles.

The smaller size of particles had a monodentate and a chelating bidentate of acetate and a hydroxy group while the large size of particles had a chelating and bridging bidentate. There are a lot of edges on the particles of the smaller size. The monodentate of acetate and the hydroxy group is adsorbed

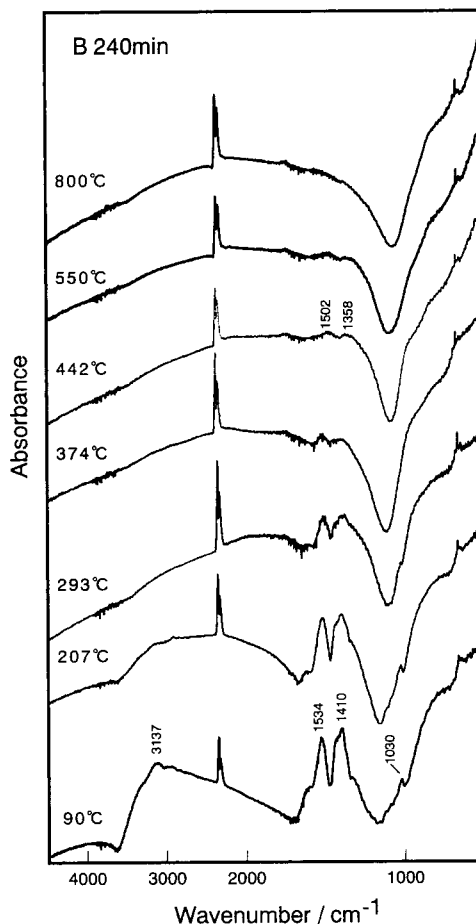
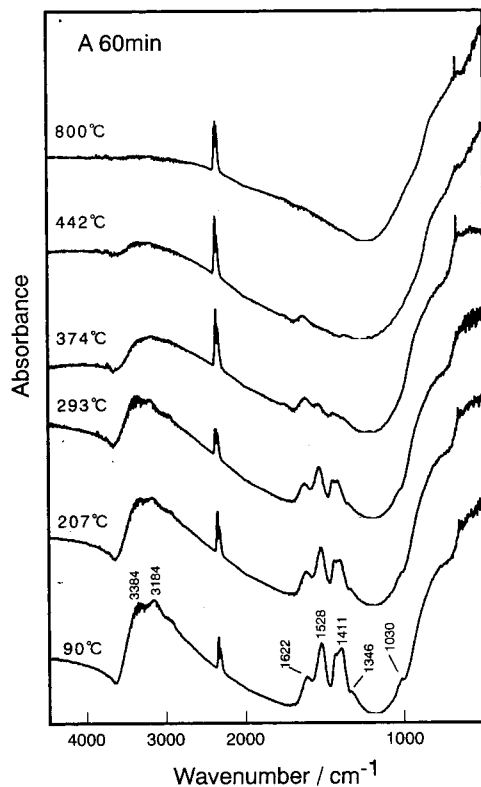


Figure 6. Infrared absorption spectra of dried and heated powders of titanium oxide prepared by a control with acetic acid in the reaction time of a catalytic sol-gel process using ammonium acetate ($[\text{Ti}(\text{C}_4\text{H}_9)_4] = 0.05 \text{ M}$, $[\text{CH}_3\text{COONH}_4] = 0.05 \text{ M}$, and $[\text{H}_2\text{O}] = 0.5 \text{ M}$). Acetic acid (8.75 mmol) was added at (A) 60 and (B) 240 min. Powders were dried at 90 °C and heated to 207, 293, 374, 442, 550, and 800 °C.

on the edge of particles. On the other hand, the larger size of particles have a much higher proportion of flat surface. The bridging bidentate is adsorbed on the flat surface of particles.

We concluded that the new ultraviolet absorption band of a sheet structure of titanium oxide was due to surface complexation with a bridging bidentate of acetate which changes the band gap of the titanium oxide surface. The bridging bidentate was formed on the flat surface of the particles of a larger lateral size ($>1\ \mu\text{m}$).

Conclusion

We succeeded in controlling the size of sheetlike particles of titanium oxide by switching off catalysis in a catalytic sol-gel process. Consequently, it can be possible to control the effects of particle size of titanium oxide on the ultraviolet absorption band. Fine control of the particle size by this method will be further developed.

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