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Paper

Synthesis of Peroxo-Modified Anatase Sol from Peroxo Titanic Acid Solution

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ペルオキソチタン酸溶液からのペルオキソ修飾されたアナターゼゾルの合成

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A peroxo titanic acid (PTA) solution has been prepared by mixing titanic acid wet gel and hydrogen peroxide solution. The PTA solution was a neutral, transparent, stable liquid. The PTA crystallized to form an anatase phase after calcination at a temperature above 250°C. When the PTA solution was autoclaved at a temperature above 100°C for 6h, it changed to a sol containing anatase crystals less than 20 nm in diameter. Aggregation occurred after autoclaving at a temperature above 120°C. When the PTA solution was heated to 100°C, it was translucent and stable in spite of containing ultrafine anatase crystals (9 nm in diameter). It was deduced that the surfaces of anatase crystals are modified by the peroxo groups.

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Key-words : *Peroxo titanic acid, Peroxo-modified anatase sol, Crystallization properties, Reaction process*

1. Introduction

Films[1] and ultrafine powders[2] of anatase have attracted much attention for use as photoelectrochemical electrodes for solar energy conversion[3] and photocatalysts for the decomposition of organic compounds.[4] Because anatase films are so useful for practical applications, they have been prepared by various methods such as chemical vapor deposition[5),6] and the sol-gel method.[1),7] In particular, the method of dip-coating by sol-gel is useful in the preparation of films on wide-area bodies and at low temperatures.

Sol-gel methods for preparing anatase films using organometallic compounds have been widely investigated.[1),7] However, these methods have several practical disadvantages. For example, the organometallic compounds used as the raw materials are expensive and intractable because they are hydrated easily with water in air. Also anatase sols prepared by these methods are unstable. In order to improve the stability of the anatase sols, acid is usually added.[1),2),7),8] However, sols with added acid cannot be applied to various materials such as metals. Therefore, the requirements for practical applications are that the raw material is a cheap inorganic compound, and the sol used to produce the anatase films is neutral, stable and can be coated onto various materials.

We have attempted to prepare thin films of metal oxides from inorganic metal solutions by a spray induction coupled plasma technique[9),10] and a spray combustion flame technique.[11] In order to prepare anatase films using these techniques, a halogen-free, nitrogen-free, stable, neutral solution of an inorganic titanic compound is required. To the best of our knowledge, however, no suitable precursor for anatase films has been reported.

We found that neutral peroxo titanic acid (PTA) solution could be derived from $TiCl_4$ solution, and transformed to a neutral, translucent sol containing peroxo-modified anatase crystals (PA sol) by heating. In the present study, the fabrication process and the properties of the PTA solution and the PA sol are examined, and the reaction process is discussed.

2. Experimental

A flow diagram for the preparation of PTA solution and PA sol is shown in Fig. 1. Titanic acid (H_4TiO_4) gel was precipitated by adding ammonia solution (1 : 9) to $TiCl_4$ aqueous solution (0.1 mol/dm^3). The final pH of the solution after precipitation was 7. The gel was washed with distilled water, and was separated by decantation and centrifugation until Cl^- ions were not detected. The titanic acid gel cake was changed to yellow, transparent PTA solution by adding excess 30 mass% H_2O_2 solution (about 4 times the number of moles of titanium). The anatase sol was obtained from the PTA solution by heating to above 100°C and holding at that temperature for 6h.

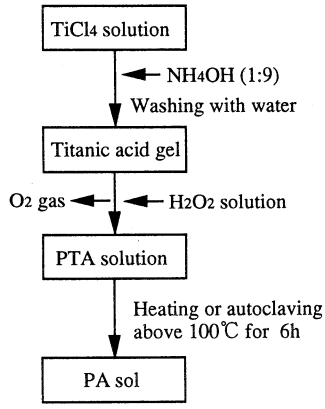

Fig. 1. A flow diagram for the preparation of PTA solution and PA sol.

The morphology of particles in the sol was observed by transmission electron microscopy (TEM). The powders obtained by drying and calcining the PTA solution and the sol were identified by powder X-ray diffraction (XRD). The crystal size was calculated using Scherrer's formula from the FWHM of the XRD peaks. Thermogravimetric (TG) and differential thermal analysis (DTA) were conducted at a heating rate of 10°C/min in air.

3. Results

3.1 Properties of PTA solution

The viscosity of the as-prepared PTA solution increased with time. It took several hours for the PTA solution to stabilize after mixing wet titanic acid gel cake and H_2O_2 solution. The final viscosity of the PTA solution was higher when the temperature of the mixed solution during the reac-

tion was high. The viscosity of the PTA solution (0.2 mol/dm^3) prepared at a constant temperature of about 30 ℃ was about 350 mPa·s. Above a concentration of 0.4 mol/dm^3, the solution became jamlike. The PTA solution was yellow, transparent and neutral (pH=6.5). The stability was so good that the properties of the solution hardly changed at room temperature over a period of 6 months. However, a flocculent precipitate was formed immediately when compounds such as acid or polyvalent metal ions were added.

The FT-IR curves for the calcined powders are shown in Fig. 2. The stretching mode frequency (890 cm^{-1}) can be used to estimate the existence of the first-order O-O bond.[12] The spectra of the PTA powders calcined at 60 and 200 ℃ showed a peak at 900 cm^{-1}, which was attributed to the peroxo group (first-order O-O bond). The spectra for the as-dried PTA and titanic acid showed broad peaks at 3200-3400 cm^{-1} due to water. The clear peak at 1630 cm^{-1} was attributed to the bending vibration of water molecules, and the peak at 1400 cm^{-1} to the stretching vibration of the N-H bonds in NH_4^+. These results suggested that NH_4^+ and Cl^- remained in the titanic acid wet gel and the PTA solution.

The XRD patterns for calcined PTA and titanic acid are shown in Figs. 3 and 4. The titanic acid crystallized to the anatase phase above 400℃, while the PTA crystallized above 250℃. It was found that PTA crystallized at a lower

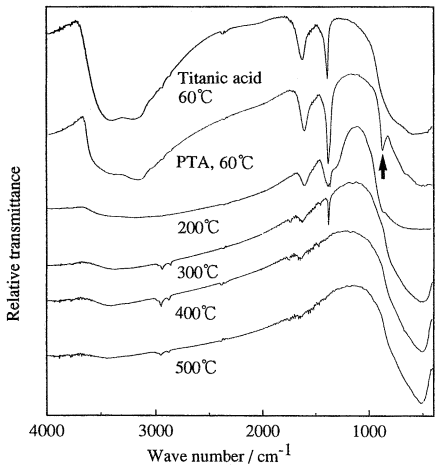

Fig. 2. FT-IR curves for powders obtained by calcining titanic acid gel and PTA solution. The arrow indicates the peak position for the first-order O-O bond.

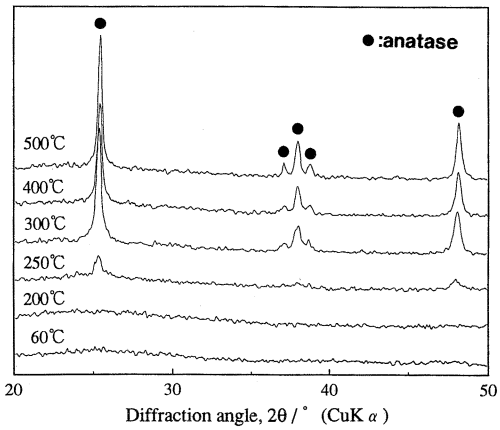

Fig. 3. XRD patterns for PTA powders calcined at different temperatures.

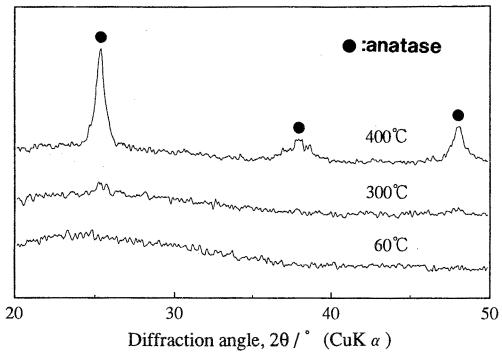

Fig. 4. XRD patterns for titanic acid powders calcined at different temperatures.

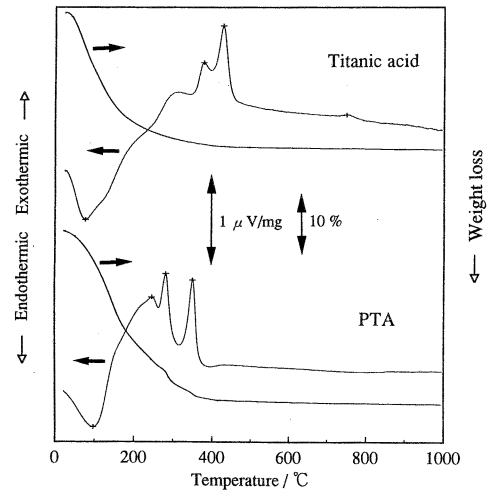

Fig. 5. TG-DTA curves for powders obtained by drying titanic acid gel and PTA solution.

temperature than titanic acid. The TG-DTA curves for as-dried powders of PTA solution and titanic acid gel as a function of temperature are shown in Fig. 5. The exothermic peak at about 350℃ is probably due to the decomposition of the remaining NH_4Cl because the temperature of sublimation and/or decomposition of NH_4Cl is about 340℃. The exothermic peaks at 250 and 280℃ for PTA are ascribed to the decomposition of the peroxo group and the crystallization to the anatase phase, while the peak at 420℃ for titanic acid is due to crystallization.

3.2 Properties of anatase sol

It is expected that PTA can be transformed to crystallized ultrafine titania by autoclaving the PTA solution which results in condensation reaction of hydroxide and peroxo groups. In fact, a sol containing crystallized anatase was obtained by heating or autoclaving the PTA solution above 100℃ for 6h. The sol obtained at 100℃ was light yellow and translucent, and it had a small viscosity (about 10 mPa·s at 0.2 mol/dm^3). The XRD patterns for the sol are shown in Fig. 6. It was found that all of the sol contained crystallized anatase. If the solution was autoclaved above 120℃, however, aggregation of the anatase sol occurred. This phenomenon is due to the decomposition of the peroxo groups indicated by the fact that the gel was no longer yellow but became a milky white aggregate. Figure 7 shows FT-IR curves for the sols obtained at 100 and 120℃. An absorption peak at 900 cm^{-1} due to peroxo groups was observed in the spectrum for the sol heated at 100℃, but no peak was observed for the sol autoclaved at 120℃.

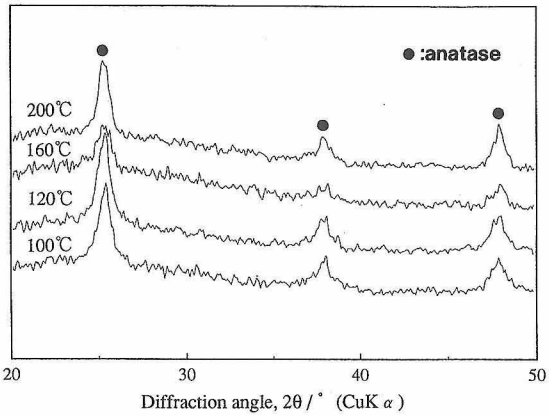

Fig. 6. XRD patterns for powders obtained by drying PA sols autoclaved at different temperatures.

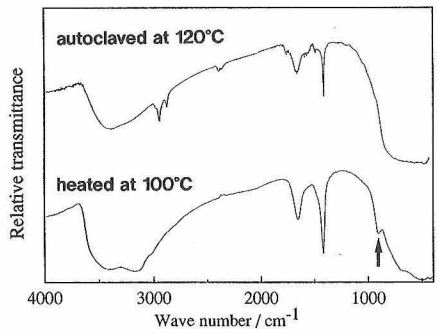

Fig. 7. FT-IR curves for sols autoclaved at 120 and 100°C. The arrow indicates the peak position for the first-order O–O bond.

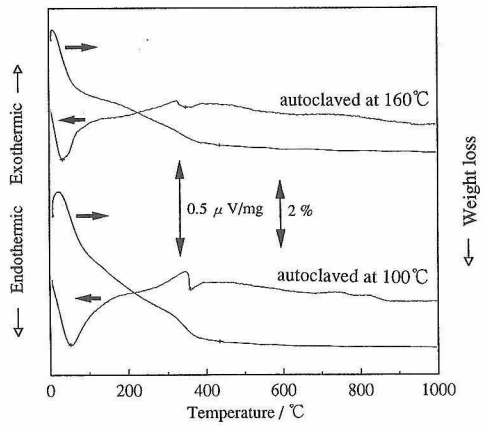

Fig. 8. TG–DTA curves for powders obtained by drying PA sols autoclaved at 100 and 160°C.

The TG–DTA curves for the as-dried powders of the sols obtained at 100 and 160°C as a function of temperature are shown in Fig. 8. The total weight loss (about 8 %) was less than that for the PTA solution (about 28 %), and no clear exothermic peak was detected for the sol. Therefore, it was deduced that all of the PTA was converted to ultrafine anatase crystals. The small peak at about 350°C may be due to the decomposition of the remaining NH_4Cl.

The TEM images of the sol are shown in Fig. 9. The sol consisted of ultrafine particles the size of most of which was below 20 nm. The particles became square with increasing treatment temperature. No change in crystal size with increasing autoclaving temperature was observed. It appeared, however, that there were many particles with sizes below 10 nm in the sols obtained at 100 and 120°C. The crystal sizes estimated from the XRD analyses were 9.0, 11, 13 and 16 nm for the sols obtained at 100, 120, 160 and 200°C, respectively. In Fig. 10, we can see the regular sequence of (101) lattice planes of anatase crystal at intervals of 0.35 nm even for the particles in the sol obtained at 100°C.

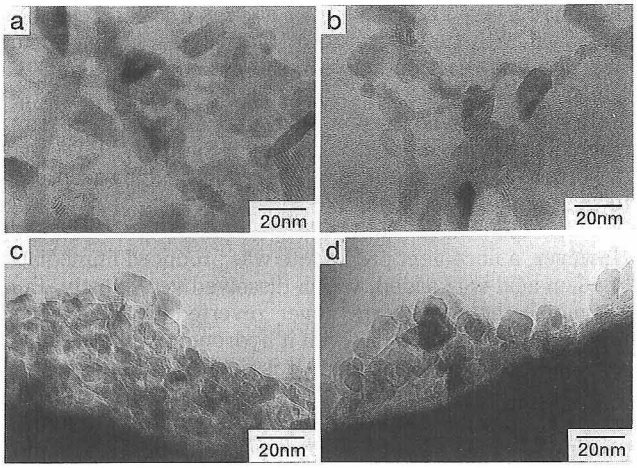

Fig. 9. Transmission electron micrographs of anatase particles in PA sols autoclaved at (a) 100, (b) 120, (c) 160 and (d) 200°C.

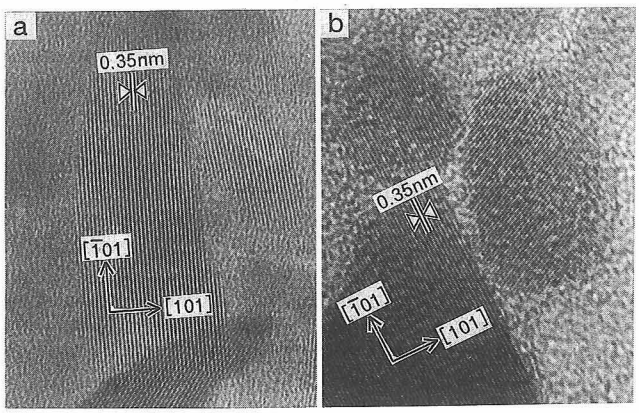

Fig. 10. Transmission electron micrographs of anatase crystals in PA sols autoclaved at (a) 100 and (b) 200°C.

Therefore, it seems reasonable to conclude that the surfaces of the anatase crystals in the sol obtained at 100°C were modified by the peroxo groups (PA sol).

4. Discussion

It has been reported that hydroperoxide groups can be formed easily on the surfaces of titanium silicate[13] and titanium dioxide[12] according to the following reactions.

$$=Ti=O+H_2O_2 \rightarrow =Ti(OH)(OOH) \quad (1)$$

$$\equiv Ti-OH+H_2O_2 \rightarrow \equiv Ti-OOH+H_2O \quad (2)$$

It has also been reported that peroxo tetra-phenylporphyrinato titanium $O_2Ti(TPP)$ is formed slowly from $OTi(TPP)$ in the presence of alkyl hydroperoxide[14] and oxo-peroxo exchange occurs in titanyl tetra-pyridylporphyrin in the presence of hydroperoxide.[15]

Based on these results, it was deduced that PTA was formed according to the following reaction.

$$=Ti(OH)_2+H_2O_2 \rightarrow =Ti(OH)(OOH)+H_2O \rightarrow =TiO_2+H_2O \quad (3)$$

The hydroxo complex, $=Ti(OH)(OOH)$, may be produced as an intermediate in the reaction, and the peroxo complex

is formed later. The viscosity of as-prepared PTA solution increased with time because of the polymerization occurring due to a reaction between the peroxo groups and the OH groups.

On the other hand, proton-assisted opening of the peroxo ring occurs when an acid is added.[14] Similarly, PTA may dissolve to form peroxide ions when acid is added according to the following reaction.

$$=TiO_2+H^+\rightarrow=TiOOH^+ \quad (4)$$

However, a flocculent precipitate was produced immediately when acid was added, which dissolved very slowly. Furthermore, the precipitate never reverted to the original transparent PTA solution even if hydroperoxide solution or ammonia solution was added. It is deduced that some species other than the ion, such as TiO(OH)(OOH), was immediately formed when the acid was added, resulting in the precipitation. However, the precipitate could not be identified.

In general, ultrafine oxide particles tend to aggregate in a neutral suspension at relatively high concentrations. However, the particles in the PA sol were well-dispersed and the viscosity was small compared to that of PTA solution. This may be due to mutual repulsion between the peroxo groups at the surface of the anatase particles, which may be negatively charged due to polarization.

5. Conclusions

It was demonstrated in this study that neutral, transparent PTA solution could be synthesized from titanic acid gel and hydrogen peroxide solution, and crystallized to form a translucent PA sol containing anatase crystals by heating at 100℃. It was deduced that the surfaces of the ultrafine anatase particles in the translucent PA sol were modified by the peroxo groups. However, above 120℃, the peroxo groups were decomposed, and aggregation of the anatase crystals occurred. The PTA solution and PA sol obtained had a number of practical advantages; e.g., they were neutral, stable liquids, the crystallization temperature was low, and the production process was easy. Therefore, PTA solution and PA sol are potential raw materials for the fabrication of titania film.

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