Growth Behavior of TiO₂ Particles via the Liquid Phase Deposition Process

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TiO₂ particles were obtained from aqueous solutions by the liquid phase deposition (LPD) method. The crystalline anatase TiO₂ particles could be prepared below 100°C directly from aqueous solutions. The growth behavior of TiO₂ particles via the LPD process was investigated by dynamic light scattering (DLS) measurement and transmission electron microscopy (TEM). From DLS measurement, the particle growth process shows a sigmoidal curve and can be divided into three stages, i.e., the initial stage, the acceleration stage, and the completion stage. TEM measurements revealed that the primary particles with a diameter of ca. 50 nm were deposited at the initial stage. At the acceleration stage, these primary particles were assembled to form raspberry-like particles with a diameter of ca. 300 nm. Finally, the particles were precipitated by further aggregation with the micrometer size at the completion stage.

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1. Introduction

TiO₂ has been studied extensively because of its wide applications in white pigments for paints,¹⁾ photocatalysts,²⁾ cosmetics,³⁾ fillers,⁴⁾ coatings,⁵⁾ and gate oxides in metal-oxide-semiconductor field emission transistor (MOS-FETs).⁶⁾ The synthesis of nanocrystalline anatase TiO₂ materials with high surface area has attracted much attention for the use in environmental remediation such as photocatalytic destruction of toxic organic compounds and inactivation of microorganisms in water and air.^{7)–9)} Controlling the crystal properties, the size and surface area, porosity is practically essential because of their potential role in enhancing the light absorbance of TiO₂ catalyst and the accessibility of reactants to the active catalytic sites.¹⁰⁾ Therefore, fabrication techniques for TiO₂ materials are important in terms of practical applications. The common procedure for the preparation of TiO₂ particles reported in the literature is based on the hydrolysis of alkoxides or chloride compounds, known as the sol-gel method.^{11)–13)} In these cases, however, high processing temperature is usually required for high crystallinity of TiO₂ particles.

Recently, fabrication techniques for crystalline inorganic materials from aqueous solutions have been focused as low-energy and environmental friendly synthesis processes.¹⁴⁾ Liquid phase deposition (LPD) method, developed by Deki et al., is one of the most versatile techniques for preparation of crystalline TiO₂ materials directly from aqueous solutions.^{15)–17)} Deposition of TiO₂ via LPD method was explained by the following mechanism:

Equation (1) is described in detail by the following two equations:

Fluoro-titanium complex ions gradually change into titanium hydroxide complex ions in an aqueous solution as shown in Eq. (3). Increase in F[−] concentration displaces the Eqs. (1) and (3) to the left-hand side, however, produced F[−] can

be scavenged by H₃BO₃ (BO₃^{3−}) as shown in Eq. (2) to displace the Eqs. (1) and (3) to the right-hand side. TiO₂ was formed from titanium hydroxide complex ions in Eq. (4), and thus the supersaturation degree and the deposition rate of TiO₂ depend on the concentration of titanium hydroxide complex ions.

In our previous work, the deposition process of anatase TiO₂ films by the LPD method was evaluated in detail.^{18)–20)} We have also demonstrated the site-selective deposition of TiO₂ films using a seed layer formed on the patterned self-assembled monolayer of silane compounds.^{18)–20)} Several other groups have reported the deposition mechanism of inorganic oxide films via the LPD process,^{15)–21)} but only few reports are found for the deposition behavior of inorganic oxide particles via the LPD method.²²⁾ In this study, we have evaluated the particle growth behavior of TiO₂ from an aqueous solution via the LPD process. Especially, the effects of incubation time and reaction temperature on the particle growth were investigated in detail. The particle size growth was examined by the dynamic light scattering technique. Transmission electron microscopy was employed for observation of the morphology of TiO₂ particles. The specific surface area of the obtained TiO₂ particles was examined by Brunauer, Emmett, and Teller (BET) analysis.

2. Experimental procedure

Unless otherwise stated all reagents and chemicals were obtained commercially and used without further purification. Ammonium hexafluorotitanate ([NH₄]₂TiF₆) was purchased from Morita Chemical Industries Co., Ltd. Boric acid (H₃BO₃; Purity 99.5%) was obtained from Kishida Chemical Co., Ltd. The water used in all experiments was deionized by a Milli-Q system. [NH₄]₂TiF₆ and H₃BO₃ were dissolved separately in deionized water at room temperature, the concentrations of the former was 0.1 mol dm^{−3} and the latter was 0.3 mol dm^{−3}. The pH of solutions was fixed to 3.8. These two solutions with equal volume were heated to the reaction temperature (40, 50, 70, 80, and 90°C) in an oil bath, and then they were mixed together. The mixture was incubated for various periods of time in an oil bath. Precipitates obtained after incubation for 24 h at 90°C were collected by the filtration and investigated using an X-ray diffractometer (XRD; RINT2000, Rigaku) with Cu Kα radiation (40 kV, 30 mA). XRD patterns

were collected by 1° per minute (measured from 10° to 90°), and counted 10 times to smooth background. A scanning electron microscope (SEM; S-3000N, Hitachi, Ltd.) at accelerating voltage of 25 kV was used to observe the morphology of precipitates. Elemental composition analysis of precipitates was performed using an energy dispersive X-ray spectroscopy (EDX) connected to the SEM. The hydrodynamic diameter of TiO₂ particles were measured by a dynamic light scattering (DLS) apparatus (ELS-8000, Otsuka Electronics). The data obtained were analyzed using the cumulant method. The structure of TiO₂ particles was examined by transmission electron microscopy (TEM). An aliquot of these dispersions was cast on a poly(vinylformal)-coated Cu grid and dried overnight. TEM observations were carried out by using a Hitachi H-800 electron microscope with an acceleration voltage of 200 kV. The sampling of TiO₂ dispersion for DLS and TEM measurements was carried out after incubation of the mixture for several periods of reaction time. The dispersion of a few microliters was diluted with the deionized water and used for DLS and TEM measurements. The specific surface area of the particles was measured using a BET surface area analyzer (CHEMBET-3000, Yuasa Ionics Inc.) after purging the sample with nitrogen gas.

3. Results and discussion

Before mixing, the both starting solutions of [NH₄]₂TiF₆ and H₃BO₃ were clear and transparent. The solution became turbid gradually after mixing of these solutions. Finally, precipitates were obtained after incubation of the mixture for a certain period of time. The reaction rate, i.e., time for the turbidity change and precipitation, depended on the reaction temperature. The higher (e.g., 90°C) the reaction temperature was, the faster the reaction proceeded and the precipitate was obtained quickly. On the other hand, the relatively long period of reaction time was required for precipitation in the case of much lower reaction temperature (e.g., 40°C). The SEM image of the precipitates prepared from the solution after incubation of the mixture at 90°C for 24 h is shown in **Fig. 1**. The particles with micrometer order in size are observed. The EDX measurement indicated that the obtained particles consisted mainly of titanium and oxygen, although a little amount of fluorine was also contained in the precipitates (figure not shown). The crystalline state of precipitates was examined by XRD measurements. **Figure 2** shows the XRD pattern of the precipitates obtained after incubation of the mixture at 90°C for 24 h. The sharp diffraction peaks assignable to anatase phase of TiO₂ are observed. This indicates that crystalline anatase TiO₂ particles could be prepared below 100°C directly from aqueous solutions. Even in other conditions (temperature and reaction time), only the peaks for anatase TiO₂ were observed (figure not shown). The sharpness and intensity of XRD patterns depends on the reaction conditions. These results suggest that the crystallinity and crystallite size changed with the change in the reaction conditions. The average crystallite size of TiO₂ was calculated according to Scherrer's equation from the (101) diffraction peak of the XRD pattern. At the initial stage of reaction (~10 min), the average crystallite size increased drastically at any reaction temperature. The increase in crystallite size converged after incubation for 20 min, and it reached ca. 16 nm when the reaction temperature was 90°C. In contrast, the average crystallite size was ca. 4 nm even after incubation for 5 h when the reaction temperature was 40°C.

From comparison of SEM observation and crystallite sizes calculated by Scherrer's equation, it seems that each TiO₂ par-

Fig. 1. SEM image of the precipitates obtained from the aqueous solution containing [NH₄]₂TiF₆ and H₃BO₃ after incubation at 90°C for 24 h.

Fig. 2. XRD pattern of the precipitates obtained from the aqueous solution containing [NH₄]₂TiF₆ and H₃BO₃ after incubation at 90°C for 24 h.

ticle is not a single crystal. Therefore, the particle growth behavior should be independent of the crystal growth. The changes in particle size of TiO₂ during the LPD process were monitored by DLS measurements. **Figure 3** shows the time dependence of hydrodynamic diameter of TiO₂ particles prepared upon incubation of the solution at various temperatures (40, 50, 70, 80, and 90°C). It is found that the particle growth rate strongly depended on the reaction temperature. The particle size rapidly reached 2 μm at 90°C (within 10 min), whereas it needed ca. 90 min in the case of 40°C. Slow increase in particle size was observed in the initial stage of reaction followed by a gradual size increase acceleration showing a sigmoidal curve. Interestingly, this trend was found at all reaction temperatures in the present study. This result indicates that the particle growth of TiO₂ in LPD process has three stages, i.e., the initial stage, the acceleration stage, and the completion stage. TEM measurements were adopted to investigate the detailed morphology of TiO₂ particles at each stage of the LPD process. TEM images of TiO₂ particles prepared upon incubation of the solution at 80°C are shown in **Fig. 4**. The spherical particles are observed for the sample obtained after incubation for 4 min (**Fig. 4a**). This period of reaction time corresponds to the induction period found in DLS (**Fig. 3**). The average particle size was ca. 50 nm and this value almost

coincides with the result of DLS measurement. The image for the sample obtained after incubation for 8 min also shows the presence of particles. The spherical particles with a diameter

Fig. 3. Time dependence of hydrodynamic diameter of TiO_2 particles prepared upon incubation of the solution at various temperatures (40, 50, 70, 80, and 90°C).

of ca. 50 nm, same as Fig. 4a, are still observed. In addition, much larger particles are observed (Fig. 4b). The average diameter of larger particles was ca. 300 nm. The feature of these particles was different from the smaller particles. The particles do not have simple spherical structure. Each particle has raspberry-like structure (the inset of Fig. 4b). This result suggests that the larger particles were formed by the assembly of primary particles found in Fig. 4a. This period of reaction corresponds to the acceleration stage found in DLS measurement (Fig. 3). Therefore, the particle growth in this stage occurred by the assembly of primary particles but not by a simple growth process. The average particle size obtained by DLS also coincides with the size of the raspberry-like particles. After incubation for 18 min (i.e., at the completion period), TEM observation revealed further aggregation of the raspberry-like particles (Fig. 4c). The aggregated precipitates have micrometer size. It also well-agreed with the DLS result. **Figure 5** shows the TEM images of TiO_2 particles obtained after incubation at 50°C and 90°C . It is noteworthy that the particle morphology shows the similar trend as the case of 80°C even the sample was prepared at 50 or 90°C . The particles obtained at 90°C for 4 min (the acceleration stage in DLS), the raspberry-like particles with the diameter of 300–500 nm were observed (Fig. 5a). After incubation for 17 min at

Fig. 4. TEM images of TiO_2 particles prepared upon incubation of the solution at 80°C for (a) 4 min, (b) 8 min, and (c) 18 min.

Fig. 5. TEM images of TiO_2 particles prepared upon incubation of the solution at (a) 90°C for 4 min, (b) 90°C for 17 min, and (c) 90°C for 27 min.

Table 1. BET Surface Area and Diameter of TiO₂ Particles

	Averaged diameter / nm	BET surface area / m ² g ⁻¹
Precipitates obtained at 90 °C for 8 min	1650	44
AMT-600 ^{a)}	30	52
TITANIX JA-1 ^{a)}	180	9

^{a)} Tayca Corporation.

90°C (the completion period in DLS), the particles formed larger aggregates with micrometer size similar to the sample obtained at 80°C for 18 min (Fig. 5b). In contrast, the spherical particles were observed even after incubation for 27 min when the reaction temperature was 50°C. This condition corresponds to the initial stage in DLS. Therefore, these results indicate that the three stages found in DLS measurements are involved in different manners of particle growth. Primary particles are first formed and deposit in the initial stage. Then in the acceleration stage, the primary particles are assembled to form raspberry-like particles. Finally in the completion stage, the particles become precipitated by further aggregation with micrometer size. Interestingly, the sizes of the primary particles and the raspberry-like particles do not depend on the reaction temperature and are maintained ca. 50 nm and ca. 300 nm, respectively.

The specific surface area of the TiO₂ particles obtained after incubation at 90°C for 8 min was determined from nitrogen adsorption-desorption isotherm and summarized in Table 1. For comparison, the specific surface areas of commercially available TiO₂ particles were also measured. The BET surface area for the obtained sample was 44 m² g⁻¹. This value is relatively high since it is comparable to that of commercial TiO₂ nanoparticles with diameter of ca. 30 nm. It can be attributed to our finding that the TiO₂ particles obtained by this process do not have simple spherical shape, but have higher-order hierarchical structure constructed by the assembly of nanoparticles.

4. Conclusions

The growth behavior of TiO₂ particles obtained from an aqueous solution via the LPD method has been evaluated in detail. The crystalline anatase TiO₂ particles could be fabricated below 100°C directly from aqueous solutions. The particle growth behavior of TiO₂ in this process was investigated by DLS and TEM measurements. The time course changes of the hydrodynamic diameter of TiO₂ particles show sigmoidal curves at all reaction temperatures in the present study. The process can be divided into three stages, i.e., the initial stage, the acceleration stage, and the completion stage. TEM measurements revealed that the spherical primary particles with a diameter of ca. 50 nm are generated in the initial stage. Then in the acceleration stage, these primary particles are assembled to form raspberry-like particles with a diameter of ca. 300 nm. Finally, the particles are precipitated by further aggregation with micrometer size in the completion stage. Even though the particle growth rate depends on the reaction temperature, the trend of the growth feature of TiO₂ particles is common at all

reaction temperatures. Interestingly, the sizes of the primary particles and the raspberry-like particles are maintained ca. 50 nm and ca. 300 nm, respectively. The obtained TiO₂ particles have relatively large specific surface area due to their higher-order hierarchical structure. Therefore, the LPD method has a large potential for the preparation of TiO₂ particles for practical applications, e.g., photocatalyst, as low-energy and environmentally friendly process.

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