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Preparation of Titania Spheres Consisting of Anatase Nanocrystals via Hydrolysis of Chemically Modified Alkoxides under Solvothermal Conditions

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Formation of anatase spheres was achieved via hydrolysis of $Ti(OC_3H_7^i)_4$ modified with acetylacetone (acac) under solvothermal conditions at 150 °C. The reduction in the degree of hydrolysis by the modification of $Ti(OC_3H_7^i)_4$ with acac led to the formation of a spherical shape. The 1–5 µm in diameter spherical particles consisted of anatase nanocrystals below 10 nm in size.

Spherical particles consisting of crystalline titania are receiving attention for applications in building units of photonic crystals,[1–11] photocatalyst,[12,13] pigments or paper whiteners,[14] and optical coatings.[15] Homogeneous shape and size and high refractive indices are suitable for the application to photonic crystals. In photocatalyst, high crystallinity and large surface area are required for the high catalytic activity, and large particle size is desired for the separation from the processed materials. Pigments and whiteners need high dispersity and color strength.

Several methods have been proposed for the preparation of titania spheres.[1–15] Monodispersed colloids of 3–6 nm in radius have been synthesized by using $Ti(OC_3H_7^i)_4$ modified by acetylacetone as a precursor.[9] Stable colloidal dispersion of titania spheres of 1–4 µm in diameter was prepared by hydrolyzing $TiCl_4$ in the presence of sulfate ions at elevated temperatures.[10] Synthesis of crystalline micron spheres of 25–30 µm of titania was achieved by thermal plasma oxidation of TiC. Titania spherical particles of 200–500 nm in diameter were produced by slow hydrolysis of titanium glycolate precursors.[2] All of these methods require firing for crystallization of titania. On the other hand, crystallization of titania without firing was achieved through several solution routes. Anatase titania prepared at near room temperature was reported using aqueous solutions of $(NH_4)_2TiF_6$[16] and TiF_4.[17–19] Rutile titania films were prepared by aging the solution of $TiOSO_4$ at 60 °C.[20,21] However, the concurrently achievement of the formation of spherical particles and the crystallization of titania at low temperature has not been achieved so far.

Here, we address the preparation of crystalline titania spheres via hydrolysis of titanium tetraisopropoxide ($Ti(OC_3H_7^i)_4$) with acetylacetone (acac) under solvothermal condition at 150 °C. The chelation of $Ti(OC_3H_7^i)_4$ by acac controlled the nucleation and growth process of titania crystals. Titania spheres of 1–5 µm consisting of anatase nanocrystals were obtained by adjusting the mole ratios, acac/$Ti(OC_3H_7^i)_4$ and $H_2O/Ti(OC_3H_7^i)_4$.

A starting solution of molar compositions, $Ti(OC_3H_7^i)_4$:i-C_3H_7OH:H_2O:acac = 1:20:2:x ($x = 0$ or 2), was prepared by the following procedure. First, acac was added to half the volume of i-C_3H_7OH, and then a mixture of the remaining i-C_3H_7OH and $Ti(OC_3H_7^i)_4$ was added to the solution with stirring. Deionized water was gradually added to the alkoxide solution under stirring. 40 cm^3 of the solution thus obtained was solvothermally treated at 150 °C in a Teflon-lined stainless steel autoclave (75 cm^3, Flon Industry, Tokyo, Japan) for 24 h. The precipitates obtained were centrifuged at 1000 rpm for 3 min, followed by washing with C_2H_5OH and drying at room temperature for 24 h.

The crystalline phases were identified by X-ray diffraction (XRD) measurement in ordinary $2\theta/\theta$ mode using an X-ray diffractometer (Model Rint 2550V, Rigaku, Tokyo, Japan) with Cu Kα radiation operated at 40 kV and 300 mA. The microstructure of the products was observed using a field emission scanning electron microscope (FE-SEM) (Model JSM-6500F, JEOL, Tokyo, Japan). Thermogravimetric and differential thermal analyses (TG-DTA) curves were obtained on the products at a heating rate of 10 °C min^{-1} in flowing air using a thermal analyzer (Model ThermoPlus 2, Rigaku, Tokyo, Japan). Infrared (IR) absorption spectra were measured with a Fourier transform infrared (FTIR) spectrophotometer (FT/IR-410, Jasco, Tokyo, Japan), using in KBr.

White precipitates were rapidly produced from the solution of $x = 0$ after the addition of H_2O at room temperature. When acac was added at $x = 2$, a transparent yellow solution was formed, where the yellow color may result from the chelation of the alkoxide molecule with acac.[22] White precipitates were obtained by the solvothermal treatments of the solution of $x = 2$ at 150 °C for 24 h. Figure 1 shows the SEM images of the products prepared from the solution of $x = 0$ and 2. Nonuniform aggregates consisting of nanoparticles below 100 nm in size were obtained from the solution without acac ($x = 0$), as shown in Figures 1a and 1b. On the other hand, the addition of acac ($x = 2$) led to the formation of spherical particles of 1–5 µm in diameter (Figures 1c and 1d). The spheres were found to consist of fine particles below 100 nm in size as shown in Figure 1e. The spherical particles were not hollow but dense as was evidenced in the SEM image of the fractured particles (Figure 1f).

Figure 2 shows the XRD patterns of the products prepared via hydrolysis under solvothermal conditions at 150 °C. The diffraction peaks attributed to anatase were detected for $x = 0$ and 2. The crystallite sizes of the anatase prepared at $x = 0$ and 2, which were calculated with Scherrer's formula, were ca. 15 and 5 nm, respectively, indicating that acac suppresses the crystal growth during the solvothermal treatment. Léaustic et al. synthesized monodisperse anatase colloids of 3–6 nm in radius by using $Ti(OC_3H_7^i)_3$(acac) as a precursor.[9] These suggest that homogeneous nucleation and growth take place during the solvothermal treatment, where the degree of hydrolysis and crystal growth are suppressed by the modification of $Ti(OC_3H_7^i)_4$ with acac.

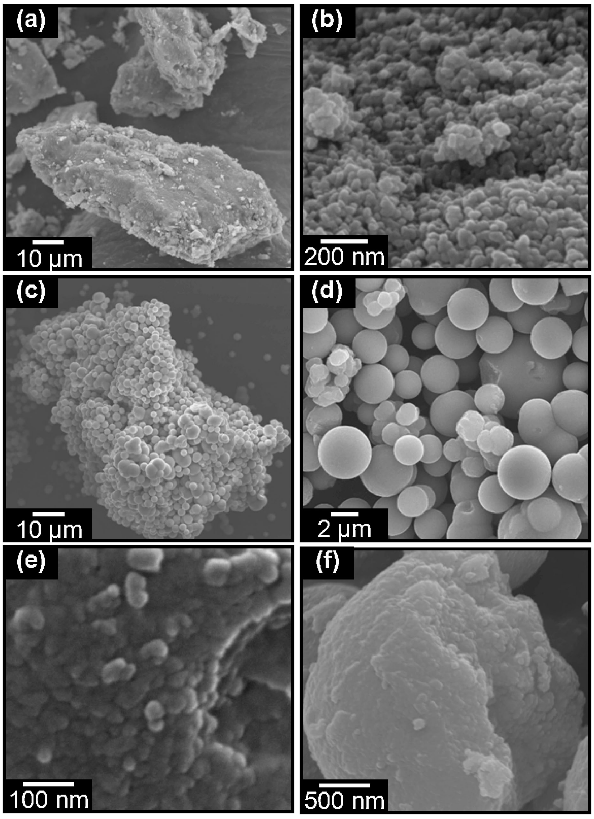

Figure 1. SEM images of the products prepared from the solutions of $x = 0$ (a and b) and 2 (c–f) via solvothermal treatment at 150 °C.

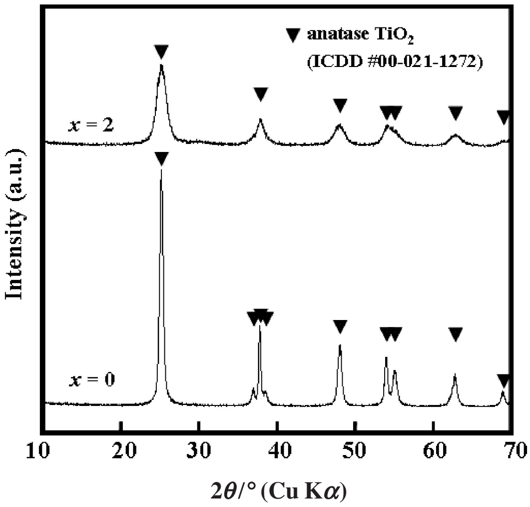

Figure 2. XRD patterns of the products prepared from the solutions of $x = 0$ and 2 via solvothermal treatment at 150 °C.

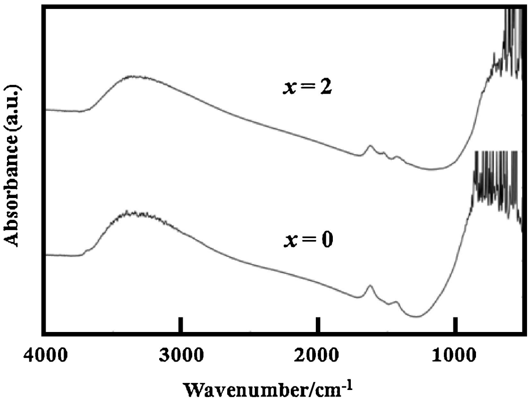

Figure 3. IR absorption spectra of the products prepared from the solutions of $x = 0$ and 2 via solvothermal treatment at 150 °C.

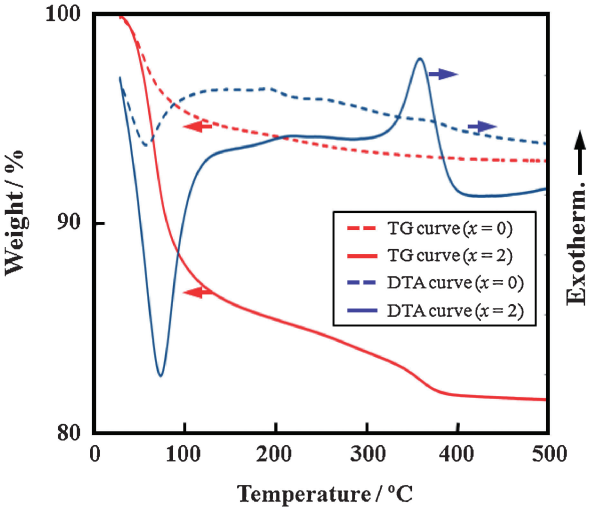

Figure 4. TG-DTA curves of the products prepared from the solutions of $x = 0$ and 2 via solvothermal treatment at 150 °C.

The inclusion of acac as well as isopropyl groups in the anatase spheres is revealed in the IR absorption spectra. The IR absorption spectra are shown in Figure 3 for the products obtained at $x = 0$ and 2. In both cases, the bands at around 600, 1450, 1630, and 3400 $\mathrm{cm^{-1}}$ were detected. The broad band at around 3400 $\mathrm{cm^{-1}}$ and the band at 1630 $\mathrm{cm^{-1}}$ are assigned to the stretching and bending vibrations of adsorbed H_2O, respectively. The broad band at around 600 $\mathrm{cm^{-1}}$ may be the envelope of the phonon bands of Ti–O–Ti bonds. The band of isopropyl groups is found at 1450 $\mathrm{cm^{-1}}$. The bands at 1540 $\mathrm{cm^{-1}}$ detected in the spectrum of $x = 2$ is assigned to the enol form of acac, which chelates $\mathrm{Ti(OC_3H_7{}^{i})_4}$.

The inclusion of acac as well as isopropyl groups is also revealed in the TG/DTA curves. Figure 4 shows the TG/DTA curves of the products obtained at $x = 0$ and 2. The first weight loss at temperatures below 100 °C indicates the evaporation of solvents (i-C_3H_7OH and H_2O). The removal of unhydrolyzed isopropoxide ligands was observed at 100–400 °C. An exothermic peak accompanied by weight loss at 300–400 °C observed in the DTA curve of $x = 2$ is attributed to the burning of acac. Such an exothermic peak was not detected at $x = 0$.

As mentioned above, the organic species remaining in the spheres is thought to suppress the crystal growth during the solvothermal treatment. This raises the question of how the spherical particles are formed at $x = 2$. In the case of $x = 0$, rapid hydrolysis of $\mathrm{Ti(OC_3H_7{}^{i})_4}$ at room temperature led to the immediate precipitation of the nonuniform aggregates. On the other hand, the chelation of $Ti(OC_3H_7{}^i)_4$ by acac provides a slow hydrolysis and homogeneous nucleation of anatase crystals of ca. 5 nm in size during the solvothermal treatment. Acac remainig on the surface of the anatase nanocrystals, as well as isopropoxy groups, makes the crystals hydrophobic. The phase separation between such hydrophobic anatase nanocrystals and the hydrophilic solvents could lead to the gradual aggregation of the nanocrystals and result in the formation of the secondary particles with the regular spherical shape.

In summary, we successfully prepared 1–5 µm titania spheres via hydrolysis of $Ti(OC_3H_7{}^i)_4$ in association with acac under solvothermal conditions at 150 °C. The spheres consisted of anatase nanocrystals below 10 nm in size. This synthetic method would be useful for the fabrication of spherical anatase particles, where control of the monodispersivity is needed.

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