

## Preparation of Colloidal Anatase TiO<sub>2</sub> Secondary Submicroparticles by Hydrothermal Sol-Gel Method

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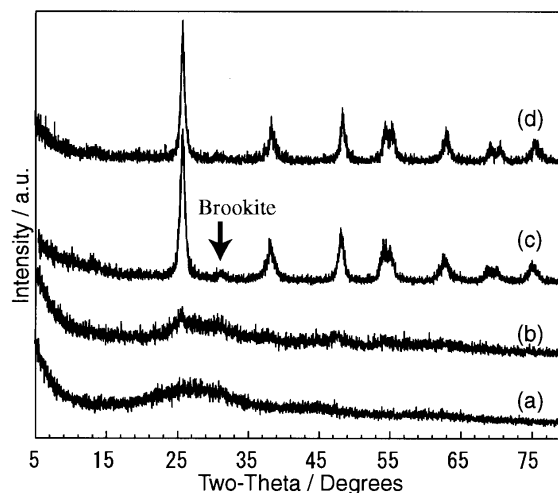
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(Received September 21, 1999; CL-990810)

Anatase TiO<sub>2</sub> nanoparticles giving stable colloids of tightly aggregated secondary particles were prepared by a hydrothermal sol-gel method. The average sizes of the primary and secondary particles, as estimated by TEM and DLS, were ca. 10 nm and ca. 100 nm, respectively. These particles were dispersed milky-whitely in water without any surfactant or polymer.

TiO<sub>2</sub> particles have received much attention for use in optoelectronic devices, sensors, and photocatalysts, in view of their chemical stability, high refractive index, and high dielectric constant.<sup>1</sup> It has been shown that anatase TiO<sub>2</sub> exhibits higher activity for oxidation of organic compounds than the other TiO<sub>2</sub> phases.<sup>2</sup> Hydrothermal treatment yields non-aggregated anatase nanocrystals in water with dispersants such as acids, bases and chelating agents, which were added before hydrothermal treatment.<sup>3</sup> On the other hand, without such dispersants the anatase monodispersed nanoparticles were grown slowly to 11 nm at 180 °C for 96 h.<sup>4</sup> Organic routes such as HyCOM (hydrothermal crystallization in organic media)<sup>5a</sup> and THyCA (transfer hydrolytic crystallization in alcohols)<sup>5b</sup> can be used for the preparation. In contrast, to use anatase particles in catalysts and green TiO<sub>2</sub> for films, secondary crystallized submicroparticles have more prospects than smaller monodispersed nanoparticles. First, although light scattering is higher for submicroparticles than nanoparticles,<sup>6</sup> the former will have as large a surface area as nanoparticles and hence may yield superior efficiency in photocatalysis.<sup>7</sup> Second, larger pores in thick films between large particles enable minimization of film shrinkage from the capillary force leading to crack formation during sintering.<sup>8</sup>

Recently, secondary anatase TiO<sub>2</sub> submicroparticles whose diameter was over 200 nm have been fabricated by hydrothermal treatment in a large amount of organic solution.<sup>9</sup> XRD and TEM measurements showed that the secondary particles thus prepared were loosely connected with each other and their colloidal stability was not described. It was reported, however, that the maximal size of secondary particles is ca. 100 nm to give a stable colloid without any surfactant or polymer.<sup>10</sup> Therefore, to obtain catalysts and green TiO<sub>2</sub> as colloidal particles, the TiO<sub>2</sub> diameter is preferred to be ca. 100 nm. In the present work, we synthesized colloidal anatase secondary particles with an average diameter of ca. 100 nm by a hydrothermal treatment in a large amount of water without any polymer, surfactant, acid or base, and after the hydrothermal treatment a nitric acid treatment was carried out to disperse the anatase particles into water. It was confirmed by transmission electron micrographs (TEM), X-ray diffraction (XRD), dynamic light scattering (DLS) and the specific surface area measurements that the primary nanocrystals were connected tightly to one another in the secondary particles.

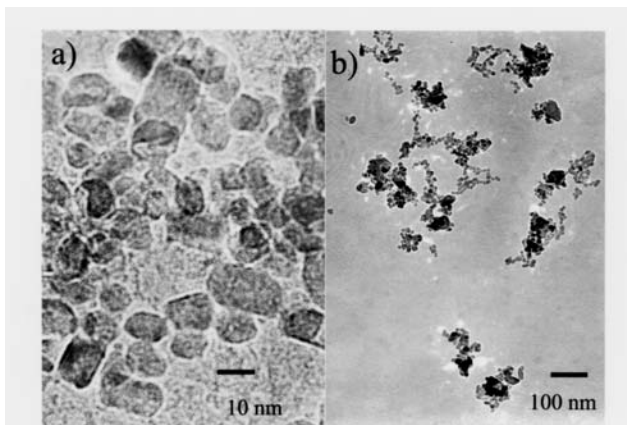


**Figure 1.** XRD patterns of TiO<sub>2</sub> particles, (a) just after hydrolysis, (b) kept for 4 weeks at room temperature, (c) just after autoclaving, (d) heated 8 h with nitric acid after autoclaving. All the prominent peaks in (d) are from anatase.

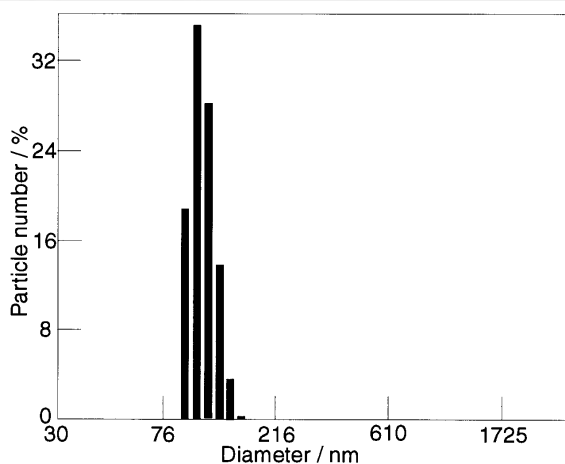
The secondary particles were prepared as follows. First, a mixture of 10.5 mL of Ti(OCH(CH<sub>3</sub>)<sub>2</sub>)<sub>4</sub> and 2 mL of 2-propanol was added dropwise to 63 mL of H<sub>2</sub>O under vigorous stirring at room temperature and then stirred for 30 min. The gel suspension thus obtained was transferred to an autoclave for hydrothermal crystallization at 235 °C for 12 h and then 0.48 mL of HNO<sub>3</sub> was added to the supernatant and precipitate. The supernatant and precipitate were heated at 80 °C for 8 h, dried in a rotary evaporator until the precipitate became powdery and finally the crystalline residue of the TiO<sub>2</sub> powder was added to ca. 4 mL of water and dispersed finely and easily. The resulting colloid was milky white and had low water-like viscosity without any surfactant or polymer. The colloids of TiO<sub>2</sub> secondary particles did not gel for several weeks.

Figure 1 depicts XRD patterns of the powder at room temperature. The precipitate just after hydrolysis was amorphous (Figure 1a), which gave rise to peaks indicating anatase and brookite after standing for 4 weeks (Figure 1b). As this material changes into crystals in this manner at room temperature, the precipitate just after hydrolysis of mixing titanium alkoxide with water was very unstable and had a high activity. After hydrothermal treatment, dominant peaks for anatase and weak peaks for brookite were observed (Figure 1c). Heating at 80 °C for 8 h with nitric acid led to weakening the brookite peak (Figure 1d). Hence, it was confirmed that the anatase nanoparticles were obtained by the hydrothermal treatment in an autoclave.

The diameters measured by TEM, XRD and the surface area measurements are comparable.<sup>3,4,9</sup> The crystallite size ( $d_{\text{XRD}}$ ) was 37 nm as calculated from the half-height width of



**Figure 2.** Transmission electron micrographs of (a) primary and (b) secondary particles.



**Figure 3.** Number-based particle size distribution determined by dynamic light scattering.

the (101) diffraction peak of anatase (Figure 1d) by the Scherrer equation with a value of the shape factor  $K$  set at 0.9. The TEM images are shown in Figure 2. The average size of primary particles ( $d_{\text{TEM}}$ ) was ca. 10 nm (Figure 2a), and the nanoparticles aggregated in dispersible secondary particles (Figure 2b). The diameter of colloidal anatase in water was determined by DLS. As shown in Figure 3, the average diameter was ca. 100 nm, which is considered to arise from the secondary particles. The specific surface areas, measured by a method of nitrogen adsorption, were 186 and 101 m<sup>2</sup>/g before and after the hydrothermal treatment, respectively. The particles were roughly spherical, hence the surface area ( $S$ ) and the diameter ( $d$ ) are correlated by the equation,  $S = 6/d\rho^3$ , where  $\rho$  (= 3.89 g/cm<sup>3</sup>) is the density of anatase. The diameters of TiO<sub>2</sub> particles calculated from this equation was 8.3 and 15.2 nm ( $d_{\text{SUR}}$ ) before and after the hydrothermal treatment, respectively. By the hydrothermal treatment, amorphous TiO<sub>2</sub> changed into the anatase crystals. The size of TiO<sub>2</sub> particles increased from 8 nm just after hydrolysis to 15 nm ( $d_{\text{SUR}}$ ) or 10 nm ( $d_{\text{TEM}}$ ) after the hydrothermal treatment, respectively. It is considered that the coaptation is formed between neighboring primary particles during crystal growth and therefore  $d_{\text{SUR}}$  is larger than  $d_{\text{TEM}}$ . Without any dispersant added the monodispersed nanoparticles were grown slowly to 11 nm at 180 °C for 96 h by hydrothermal treatment.<sup>4</sup> It hence appears that when

nanoparticles are caused to grow rapidly at a high temperature (235 °C) the coaptation is formed between them immediately, but that the connections between the secondary particles are so weak that they are broken by heating with HNO<sub>3</sub>. Therefore, probably because the connection between the primary particles is strong in the present work, the secondary particles disperse keeping their frames.

It is generally noted that the correlation among the diameters  $d_{\text{XRD}}$ ,  $d_{\text{TEM}}$  and  $d_{\text{SUR}}$  is fairly good.<sup>3,4,9</sup> In the present work, however, the diameters of the TiO<sub>2</sub> crystals were smaller in the order  $d_{\text{XRD}} > d_{\text{SUR}} > d_{\text{TEM}}$ . In particular,  $d_{\text{XRD}}$  was substantially larger than  $d_{\text{SUR}}$  and  $d_{\text{TEM}}$ . In the dark images of TEM, however, no continuation of crystal structure among the primary particles was observed. We suppose that there exist large crystals formed from some primary particles, and that the other primary particles are connected with some inter-particle space maintained.

The stable-colloidal anatase submicroparticles which comprised the hard inter-connected primary particles were obtained by a hydrothermal sol-gel method. Such unique particles have not been reported yet. This result may prove useful to synthesize colloidal anatase particles for fabrication of photocatalysts and porous thick films.

The authors are indebted to Mr. T. Tsuru for the specific surface-area measurements and to Mr. G. Katano and Mr. K. Ueyama for the TEM observations (Institute of Industrial Science, The University of Tokyo).

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