Synthesis of nanocrystal assembled TiO$_2$ particles by boric acid free liquid phase crystal deposition

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Anatase TiO$_2$ particles consisted of nanocrystals were successfully fabricated in boric acid free aqueous slutions. They showed X-ray diffraction peaks of single phase of anatase TiO$_2$ and were about 100–200 nm in diameter in scanning electron micrographs. Transmission electron microscopy analysis indicated high crystallinity and unique morphology of the particles. Liquid phase crystal deposition method was improved on the viewpoint of the boric acid free system. The particles can be applied to not only electronic devises, optical devices and photocatalysts, but also cosmetics, food additives and pharmaceutical products.

1. Introduction

TiO$_2$ nanoparticles are of interest for catalysts,[1] photocatalysts,[2]-[4] gas sensors,[5],[6] lithium batteries,[7]-[9] biomolecular sensors,[10]-[12] dye-sensitized solar cells,[13]-[15] cosmetics, food additives and pharmaceutical products. They have been prepared by flame synthesis,[16],[17] ultrasonic irradiation,[18],[19] chemical vapor synthesis,[20] sol–gel methods[2),21)-24) and liquid phase deposition[25)-29) of amorphous TiO$_2$. Matijevic et al. prepared titanium oxide particles from solutions containing TiCl$_4$, HCl and Na$_2$SO$_4$ at 98°C (°C=273.15 K) for 37 days.[30] Fukui et al. prepared cube-shaped hydrous titanium oxide fine particles by colloid aging methods.[31]

Recently, the aqueous solution process was developed to form nanoparticles of crystalline anatase TiO$_2$ at ambient temperatures. The solution technique called the liquid phase crystal deposition method realized anatase nanoparticle synthesize without high temperature annealing.[11),12) The particles have unique morphology and a high specific surface area, which is essential for highly-efficient photocatalysts, solar cells and sensors. Additionally, micropatterns of anatase films were prepared on low heat resistant polymer films for next generation flexible solar cells.[15]

However, toxic boric acid was included as a scavenger in the solutions. Boric acid has been considered to be indispensable for chemical reaction to form TiO$_2$. Residual boric acid has limited the variety of applications such as cosmetics, food additives and pharmaceutical products.

In this study, nanocrystal assembled TiO$_2$ particles were synthesized by a newly developed boric acid free liquid phase crystal deposition. Boric acid was shown to be dispensable for crystallization of TiO$_2$ in the liquid phase crystal deposition method.

2. Experimental

2.1 Liquid phase crystal deposition of anatase TiO$_2$

Ammonium hexafluorotitanate ([NH$_4$]$_2$TiF$_6$) (Morita Chemical Industries Co., Ltd., FW: 197.95, purity 96.0%)

was used as received. Ammonium hexafluorotitanate (2.062 g) was dissolved in deionized water (200 mL) at 90°C. The concentration of ammonium hexafluorotitanate was 0.05 M (M=mol/dm^3). The solutions were kept at 90°C for 1 h (h =3.6 ks) using a water bath with no stirring. They were then left at a room temperature of 18°C. Precipitates were washed with distilled water at 50°C three times. They were dried at 60°C for 12 h after removal of the supernatant solution.
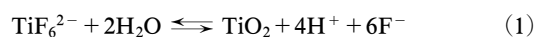
2.2 Characterization

The crystal phase of the particles was evaluated with X-ray diffractometer (XRD; RINT–2100V, Rigaku) with CuKα radiation (40 kV, 30 mA). Diffraction patterns were evaluated using JCPDS, ICSD (Inorganic Crystal Structure Database) data (FIZ Karlsruhe, Germany and NIST, USA) and FindIt. Morphology of TiO$_2$ was observed with a field emission scanning electron microscope (FE–SEM; JSM–6335FM, JEOL Ltd.) and a transmission electron microscope (TEM; JEM–2010, 200 kV, JEOL Ltd.). Weight loss of the particles and evolved gases from the particles were simultaneously analyzed with TG-DTA/mass spectrometer system (Thermo Mass, rate of temperature increase 20°C/ min, He 300 ml/min, sample weight 10 mg, m/z 10–100, interface temperature 250°C, Rigaku). Evaporation gas analyses were carried out with this system.

3. Results and discussion

3.1 Liquid phase crystal deposition of anatase TiO$_2$

The aqueous solutions containing ammonium hexafluorotitanate were transparent at room temperature. They became lightly clouded by the increase of the solution temperature. The particles were homogeneously nucleated in the solutions, turning the solutions white. In contrast, transparent ammonium hexafluorotitanate solution became clouded at room temperature by the addition of boric acid. This showed boric acid accelerated the formation of TiO$_2$ particles.[25]

Deposition of anatase TiO$_2$ proceeds by the following mechanisms in the solution containing boric acid:[25]
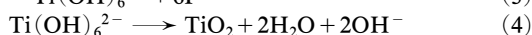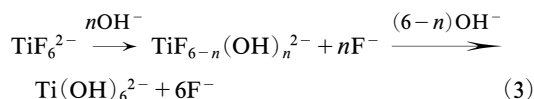
$$TiF_6^{2-} + 2H_2O \rightleftharpoons TiO_2 + 4H^+ + 6F^- \qquad (1)$$

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$$BO_3^{3-} + 4F^- + 6H^+ \longrightarrow BF_4^- + 3H_2O \qquad (2)$$

The increase of F^- concentration displaces Equation (1) to the left; however, the produced F^- can be scavenged by boric acid, H_3BO_3 (BO_3^{3-}) as shown in Equation (2) to displace Eq. (1) to the right. Therefore, boric acid has been considered to be indispensable for the chemical reaction to form TiO_2.[25]

Actually, precipitation of TiO_2 particles was not observed without boric acid at 50°C. However, Eq. (1) was shown to proceed to the right at 90°C in this study. TiO_2 particles were precipitated to cover the bottom of vessels white at 90°C.

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

$$TiF_6^{2-} \xrightarrow{nOH^-} TiF_{6-n}(OH)_n^{2-} + nF^- \xrightarrow{(6-n)OH^-}$$

$$Ti(OH)_6^{2-} + 6F^- \qquad (3)$$

$$Ti(OH)_6^{2-} \longrightarrow TiO_2 + 2H_2O + 2OH^- \qquad (4)$$

Fluorinated titanium complex ions gradually change into titanium hydroxide complex ions in an aqueous solution, as shown in Eq. (3). Anatase TiO_2 is formed from titanium hydroxide complex ions ($Ti(OH)_6^{2-}$) in Eq. (4).

3.2 Crystal phase of TiO_2 particles

X-ray diffraction peaks for the particles prepared at 90°C without boric acid were observed at $2\theta = 25.2$, 37.8, 47.7, 53.8, 54.8, 62.4, 68.6, 69.8, 74.7, 82.2, 82.5, 93.7 and 94.4° after evaluation of N_2 adsorption. They were assigned to the 101, 004, 200, 105, 211, 204, 116, 220, 215, 224, 312, 305 and 321 diffraction peaks of anatase TiO_2 (JCPSD No. 21–1272, ICSD No. 9852) (**Fig. 1**).

The 004 diffraction intensity of randomly oriented particles is usually 0.2 times the 101 diffraction intensity as shown in JCPDS data (No. 21–1272). The 004 diffraction intensity of the particles deposited in this study, was 0.24 times the 101 diffraction intensity. The integral intensity of the 004 diffraction was 0.21 times the 101 diffraction intensity. These indicated slight c-axis orientation of the particles. Particles were not oriented on a glass holder for XRD measurement. Therefore, TiO_2 crystallites were anisotropic shapes in which the crystallites were slightly elongated along the c-axis. The crystallites had a large number of stacks of c planes such as (001) planes compared to stacks of (101) planes. The diffraction intensity from the (004) planes were enhanced compared to that from the (101) planes.

On the other hand, the particles prepared at 50°C using boric acid for 30 min had strong c-axis orientation.[11),12)] The 004 diffraction intensity of the particles was 0.36 times the 101 diffraction intensity.[11),12)] The crystal growth condition such as the solution temperature would influence on c-axis orientation of the crystals.

Crystallite sizes perpendicular to (101) or (004) planes of the particles prepared at 90°C without boric acid were estimated from full-width half-maximum of 101 or 004 peak to be 36.5 nm or 39.2 nm, respectively. Slight elongation of crystallites in the c-axis direction was suggested by difference in crystallite size. Crystallite sizes were similar to that of the particles prepared at 90°C using boric acid and hydrochloric acid for 30 min (101: 26.3 nm, 004: 32.9 nm).[32)] They were, however, much larger than that of the particles prepared at 50°C using boric acid for 30 min (101: 3.9 nm, 004: 6.3 nm)[11),12)] and that of the particles prepared at 50°C using
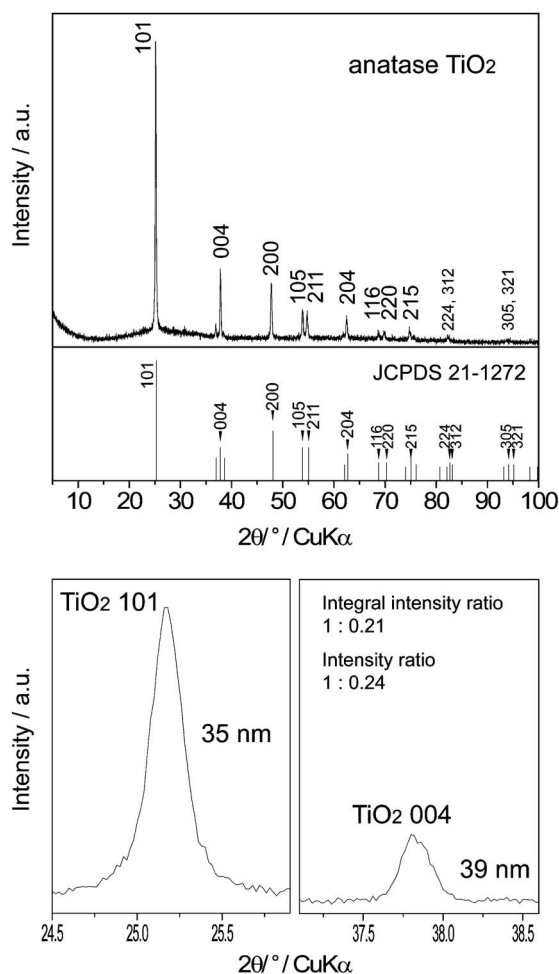

Fig. 1. XRD Diffraction Pattern of Anatase TiO_2 Particles.

boric acid for 30 min and left to cool for 1 day (101: 6.9 nm, 004: 18.5 nm).[33)] Additionally, crystallite size ratio of 004 to 101 of the particles prepared at 90°C without boric acid (1.07 = 39.2 nm/36.5 nm) was similar to that of the particles prepared at 90°C using boric acid and hydrochloric acid for 30 min (1.25 = 32.9 nm/26.3 nm),[32)] but smaller than that of the particles prepared at 50°C using boric acid for 30 min (1.62 = 6.3 nm/3.9 nm)[11),12)] and that of the particles prepared at 50°C using boric acid for 30 min and left to cool for 1 day (2.68 = 18.5 nm/6.9 nm).[33)] The crystallites prepared at 50°C have a high aspect ratio compared to that prepared at 90°C. The solution temperature had an influence on the anisotropic crystal growth of anatase TiO_2. Crystal growth would depend on temperature rather than additives such as boric acid or hydrochloride acid.

3.3 Thermal analysis and evolved gas analysis of TiO_2 particles

XRD patterns of anatase TiO_2 are similar to that of metatitanic acid ($TiO(OH)_2$ or $TiO_2 \cdot H_2O$). They can not be distinguished with XRD analysis. Metatitanic acid has H_2O of 18.4 mass% in the crystals. Thermogravimetric analysis of the particles was carried out to evaluate weight loss by the heat treatment. The weight of the particles decreased about 5% from 40°C to 240°C and about 2.8% from 240°C to
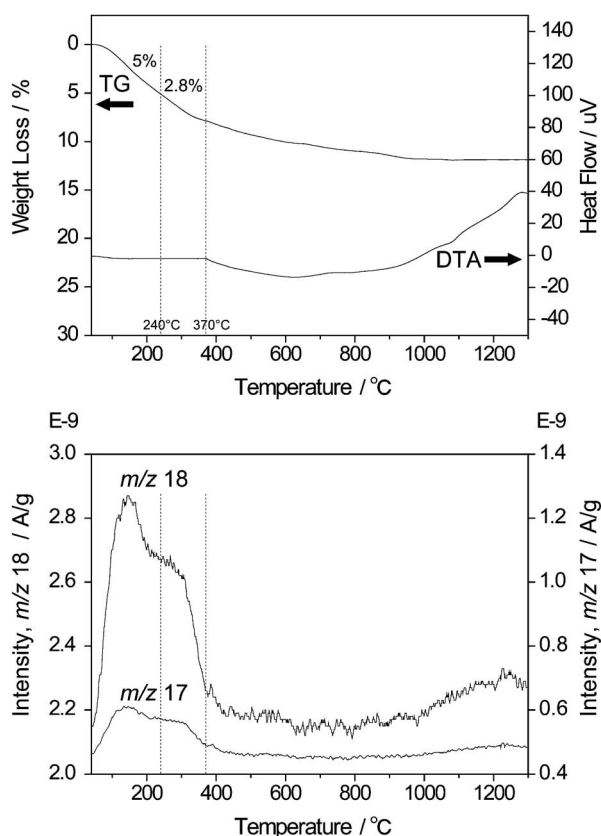
Fig. 2. Thermogravimetric analyses (upper) and evaporation gas analysis (lower) of anatase TiO_2 particles.

Fig. 3. SEM micrograph of anatase TiO_2 particles.

A strong c-axis orientation along acicular shapes was not observed clearly with TEM analysis. It was consistent with XRD evaluations. The particles prepared at 90°C for 1 h in this study had only a weak c-axis orientation. They have a different morphology from that prepared at 50°C using boric acid for 30 min[11),12)] in which a high c-axis orientation was observed with XRD and TEM. Anisotropic crystallite growth along c-axis would be sensitive to crystal growth conditions such as solution temperature. It indicated c-axis orientation and morphology of the crystallites can be easily controlled by solution conditions.

4. Conclusion

Anatase TiO_2 particles were prepared in aqueous solutions without the use of toxic boric acid. They were about 100–200 nm in diameter and have microasperity on their surfaces. Slight c-axis orientation of the crystals was observed with XRD. C-axis orientation degree was smaller than that of the particles prepared at 50°C using boric acid for 30 min. It indicated c-axis orientation and morphology of the crystals can be easily controlled by solution conditions. The liquid phase crystal deposition method was improved on the viewpoint of a boric acid free system in this study. Anatase TiO_2 particles can be applied to not only electronic devices, optical devices and photocatalysts, but also cosmetics, food additives and pharmaceutical products because there is no use of a toxic boric acid.

370°C (**Fig. 2**). Gases of m/z 18 or m/z 17, i.e., evaporation gases having a mass to charge ratio of 18 or 17, were detected from 40°C to 370°C and were assigned to H_2O. They were not observed above 370°C. DTA analysis showed a flat spectrum with no peaks from 40°C to 370°C indicating no phase transition. These analyses indicated that the as-prepared particles were anatase TiO_2 with physically adsorbed water on the surfaces. The adsorbed water can be removed by heat treatment at 370°C or higher temperatures.

3.4 Microstructure of TiO₂ particles

The particles were placed on silicon wafers after drying and observed with a SEM (**Fig. 3**). They were about 100–200 nm in diameter. Microasperity was observed on surface of the particles. They were roughly estimated to about 5–30 nm. Aggregation of the particles was also observed. TiO_2 particles which crystallized homogeneously would further grow to form aggregations in the solutions.

The particles were observed with a TEM. The particle diameter was estimated to be about 100–200 nm (**Fig. 4**a). Relief structures were observed on surfaces of the particles (Fig. 4b). The particles would be assemblies of nano crystals. They were roughly estimated to about 5–20 nm (Figure 4c). Lattice fringes were observed from nano crystals on surfaces of the particles. They were assigned to a single phase of anatase TiO_2. The Fourier transformation image of Fig. 4c showed diffraction rings (Fig. 4c). They were electron diffractions from 101 or 004 crystal faces of anatase TiO_2.
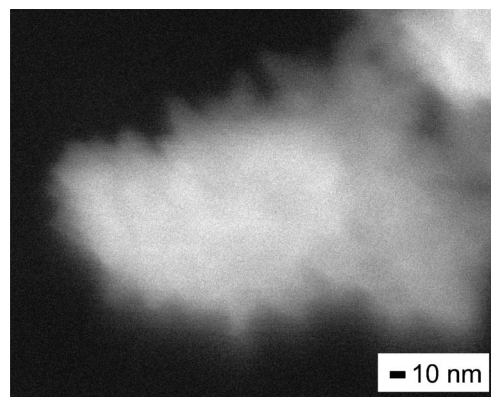
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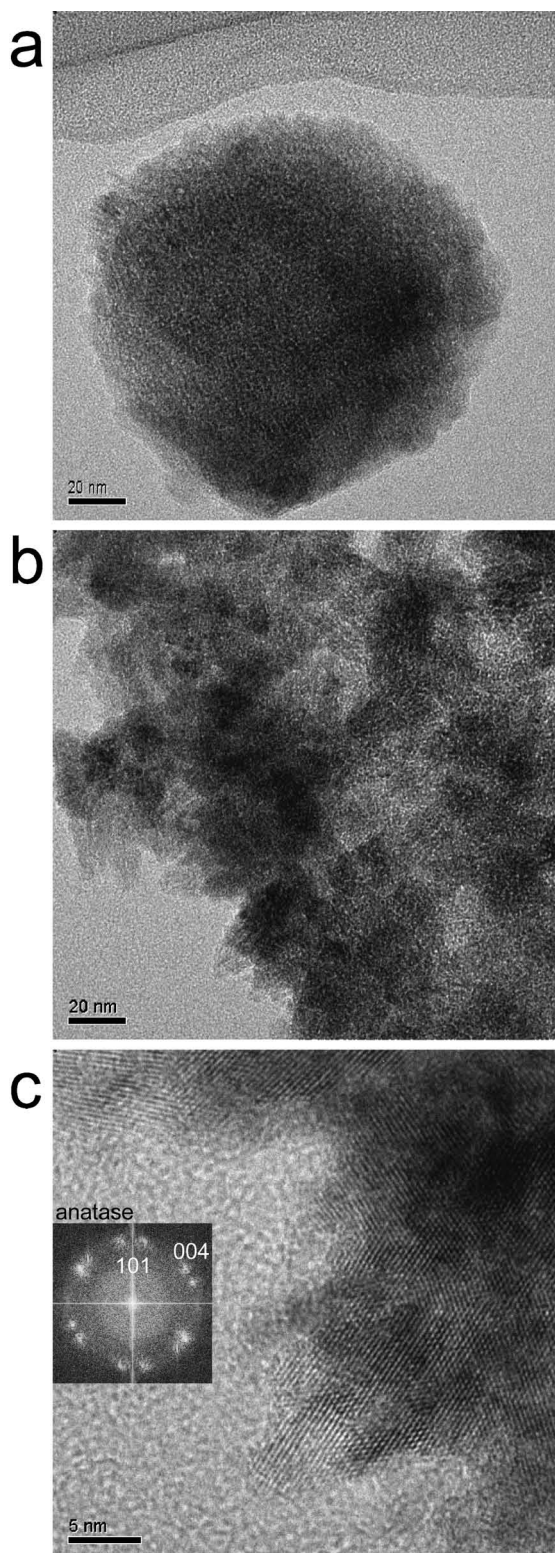8) A. S. Arico, P. Bruce, B. Scrosati, J. M. Tarascon and W. Van Schalkwijk, *Nature Mater.*, 4, 366–377 (2005).

Fig. 4. (a): TEM micrograph of anatase TiO_2 particles. (b): Magnified area of (a) showing morphology of crystals. (c): Magnified area of (a) showing lattice images of anatase TiO_2. Insertion in (c): FFT image of (c).

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