

# Phase-Compositional and Morphological Control of Titania Nanoparticles via Low Temperature Dissolution-Reprecipitation Process in Liquid Media

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Rutile or anatase nanocrystals were prepared by a "low temperature dissolution-reprecipitation process" (LTDRP) in HCl or H<sub>2</sub>SO<sub>4</sub> solutions around room temperature. The reprecipitation temperature and organic solvent addition in the solution system greatly affected the phase composition of the final powders. The phase compositional and morphological control of the final powders might be realized by applying a washing operation followed by a hydrothermal treatment in liquid media.

Nanosize particle shows quite different physico-chemical properties compared with that of bulk one.<sup>1</sup> Titania nanocrystals have attracted increasing attention because of its wide applications in many fields especially in photochemical research.<sup>2,3</sup> Usually, titania is prepared by calcination of amorphous titania gel in air at high temperature, however, besides the large environmental load, hard agglomeration and particle size increase can not be avoided. Recently, hydrothermal treatment has been applied for the crystallization of titania and other oxide powders. Some researchers reported that phase composition of titania was effected by pH value,<sup>4</sup> stirring condition<sup>5</sup> and precursor concentration<sup>6</sup> etc. Although rutile particle was reported to be prepared from aqueous TiOCl<sub>2</sub> solution at low temperature,<sup>7</sup> the morphological control of the crystalline titania was not sufficient.

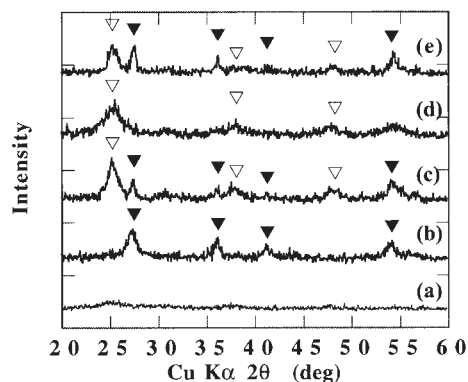
In the present study, titania crystal was prepared from titanium tetraisopropoxide precursor by the "low temperature dissolution-reprecipitation process" (LTDRP) in liquid media under milder conditions. By the new process, the thermodynamically stable rutile phase with high specific surface area and different micro-morphology can be prepared around room temperature. The phase-compositional and morphological control of the final crystalline titania are realized by changing reprecipitation temperature, adding organic solvent or applying a washing operation followed by a hydrothermal treatment. Process simplification leads to lower production costs and makes continuous process possible. In addition, low treatment temperature makes it possible to produce powders with larger specific surface area and softer agglomeration, which will strongly affect their physico-chemical aspects.

Amorphous TiO<sub>2</sub> gel was prepared by slowly adding 0.125 mol of titanium tetraisopropoxide (Kanto Chemical Co., Inc. Japan.) to 1000 cm<sup>3</sup> of distilled water at room temperature. Transparent acidic TiO<sub>2</sub> colloid solution was obtained by adding hydrochloric acid with TiO<sub>2</sub>/HCl molar ratio of 0.25 in the fresh prepared amorphous slurry and stirring at room temperature for 4 h. After aging at desired temperature (25–225 °C) for 4–48 h, fine crystals of titania were produced. The phase constitution of the products was determined by X-ray diffraction analysis (XRD, Shimadzu XD-D1). The molar ratios of anatase and rutile were determined by the XRD peak intensity ratio as<sup>8</sup>

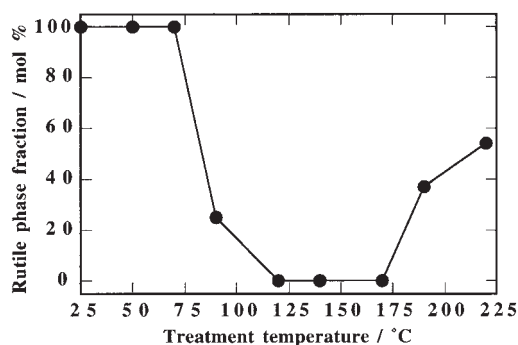
$$W_R = 1 / ((1 + 0.8(I_A/I_R))) \quad (1)$$

where  $W_R$ ,  $I_A$  and  $I_R$  are the mole fraction of rutile, the XRD peak intensity of anatase d(101) and that of rutile d(110). The specific surface areas were determined by the amount of nitrogen adsorption at 77 K (Quantachrome: NOVA 1000-TS). The microstructure of the powder was observed by transmission electron microscopy (TEM, JEOL, JEM-2000EX II) at 200 kV. The crystalline size of the powder was determined using a TEM photograph.

Figure 1 shows the XRD patterns of the amorphous titania and the crystalline titania prepared by LTDRP in HCl solution at different temperatures. It was found that amorphous titania dissolved as transparent titania gel in stirred acidic solutions, and reprecipitated after a long time (48 h) aging at room temperature or a short period (4 h) aging at higher temperatures (>60 °C). Figure 2 shows the mole fraction of rutile phase formed by LTDRP at various precipitation temperatures. The powders reprecipitated at room temperature were identified as crystalline particles by XRD and Raman analysis. The powders prepared by LTDRP in 0.5 M (1 M = 1 mol dm<sup>-3</sup>) HCl and HNO<sub>3</sub> solutions possessed rutile phase with high specific surface areas. On the other hand, the powders prepared in 0.2 M sulfuric acid possessed anatase phase with low crystallinity



**Figure 1.** XRD patterns of the powders prepared by (a) hydrolysis of titanium tetraisopropoxide in water; by LTDRP in 0.5 M HCl solution at (b) 25 °C for 48 h, (c) 90 °C for 4 h, (d) 170 °C for 4 h and (e) 220 °C for 4 h: (▽) anatase phase titania, (▼) rutile phase titania.



**Figure 2.** The mole fraction of rutile phase of titania powders formed by LTDRP at different precipitation temperature.

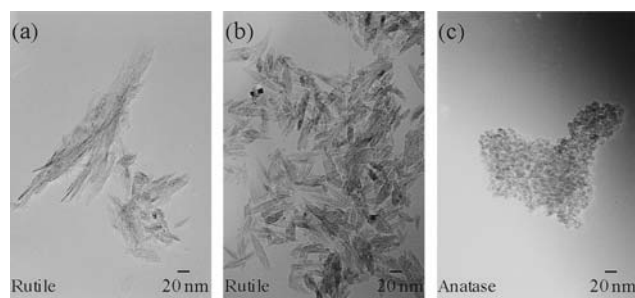
**Table 1.** Phase composition and BET specific surface area of the powders prepared under different conditions

Sample [Medium-Temp., °C]	H <sub>2</sub> SO <sub>4</sub> -25	HNO <sub>3</sub> -25	HCl-25	HCl-50	HCl-140	HCl-220	H <sub>2</sub> O-220
Phase Composition*	A	R	R	R	A	A + R	A
S.S.A./m <sup>2</sup> g <sup>-1</sup>	7.8	118.9	135.0	106.0	212.0	94.3	142.0

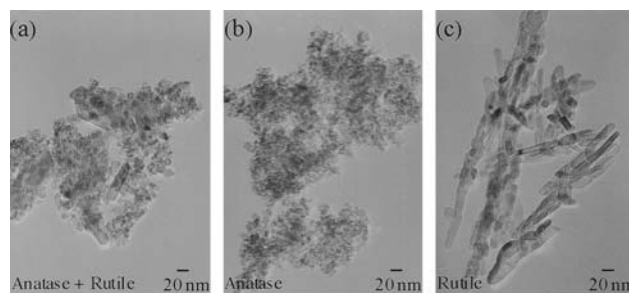
\*R: rutile phase titania; A: anatase phase titania.

and small specific surface area as 7.8 m<sup>2</sup>/g. Pure rutile phase formed between room temperature and 70 °C, and the products consisted of a mixture of rutile and anatase phase at above 70 °C. The mole fraction of rutile phase decreased with increasing treatment temperature. Pure anatase phase could be obtained above 120 °C. However, the rutile fraction increased again above 170 °C. The reason might be explained by the crystallization rate. It is known that both anatase and rutile titania can grow from TiO<sub>6</sub> octahedra, and the phase formation proceeds by the rearrangement of the octahedra. It might be suggested that thermodynamically stable rutile nuclei with compact texture formed by very slow precipitation rate at low temperature below 70 °C, on the other hand, the metastable anatase phase formed directly at higher temperature because of the larger reprecipitation rate. Above 170 °C, part of the anatase phase transformed to thermodynamically stable rutile phase. The phase composition and BET specific surface area of the prepared powders are summarized in Table 1. The powder prepared in sulfuric acid solution showed very small specific surface area. Meanwhile, the powders prepared in hydrochloric acid showed large specific surface area and the anatase phase possessed larger specific surface area than that of rutile phase. The specific surface area decreased with increasing precipitation temperature. It implied that crystalline growth occurred at higher temperature, and anatase phase possessed smaller crystalline size compared with that of rutile phase in the same reaction system. In addition, the rutile titania prepared in the present study showed smaller band gap value (3.0 eV) than that of anatase (3.1 eV).

Figure 3 shows the TEM photographs of the titania powders crystallized by LTDRP in 0.5 M HCl solution at different temperatures. The needle-like rutile powders with aspect ratio of 6 and 3.5 were obtained at 25 °C and 70 °C, respectively (Figure 3-a & b). However, pure anatase phase with spherical morphology (diam. ≈ 6 nm) was formed at 140 °C (Figure 3-c). The particle size observed from TEM photographs agreed with the result of the specific surface area in Table 1. The reprecipitation temperature significantly affected the phase and morphology of the final titania powders. In addition, the phase compositional and morphological control of the final powders also might be realized by applying a washing operation followed by the hydrothermal treatment (see Figure 4). The powders prepared by LTDRP in HCl solution at 220 °C possessed a mixture of spherical anatase and rod-like rutile phases (Figure 4-a). The hydrothermal treatment of the amorphous



**Figure 3.** TEM photographs of the powders prepared by LTDRP in 0.5 M HCl solution at (a) 25 °C for 48 h, (b) 50 °C for 4 h, and (c) 140 °C for 4 h.



**Figure 4.** TEM photographs of the powders prepared by (a) LTDRP in 0.5 M HCl solution at 220 °C for 4 h, (b) hydrothermal treatment at 220 °C for 4 h using the amorphous precursor washed with distilled water, and (c) hydrothermal treatment at 220 °C for 4 h using the precursor from LTDRP in 0.5 M HCl solution at 25 °C followed by washing with distilled water.

precursor that washed with distilled water only produced anatase phase (Figure 4-b). On the other hand, if the precursor was prepared by washing the products via LTDRP at 25 °C, rod-like pure rutile phase with high crystallinity was formed after hydrothermal treatment at the same temperature (Figure 4-c). The prepared rutile powders possessed relative large specific surface area of 65.1 m<sup>2</sup>/g. This result indicated that LTDRP and washing operation greatly affected the phase composition and morphology of the final titania powders. If the precursor was prepared by LTDRP at 25 °C without a post-washing operation, the products after the hydrothermal treatment at 220 °C just showed a mixture phase with a similar morphology to that in Figure 4-a but not the pure rutile phase with rod-like morphology. This result also implied that anatase phase was formed directly at higher temperature range from solution but not from the phase transformation of rutile, remember that rutile is a thermodynamic stable phase. It was also found that the phase composition affected by the addition of organic solvents during LTDRP. As an example, the powder prepared at 70 °C in Figure 2 showed rutile phase, while that prepared at the same conditions except by adding 25 vol% ethanol showed anatase phase. The reason why alcohol addition affects the phase composition of the final powders has not been understood and will be investigated in further study.

In a previous paper,<sup>9</sup> it has been reported that photocatalytic activity of titania strongly related to their crystallinity and specific surface area. Recently, it has been expected that rutile titania also shows excellent photochemical properties.<sup>10</sup> Thus, the anatase and rutile phase with high crystallinity, large specific surface area and different morphology prepared by LTDRP are expected to be valuable on photocatalytic applications.

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