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Effect of hydroxy and carboxy groups on anisotropic growth of rutile-type titania under hydrothermal conditions

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ABSTRACT

Control of crystal growth leads to highly functional materials with desired morphologies. In this study, the relationship between select additives and the crystal growth of rutile-type titania under hydrothermal conditions using α-hydroxy acids, carboxylic acids, or alcohols as additives was systematically investigated. Without additives, rod-like rutile crystals with average dimensions of 295 nm × 67 nm were formed. Acceleration of the crystal growth was observed and the aspect ratios of the resulting rod-like crystals were found to increase in the presence of the additives. Alcohols promoted crystal growth along the c-axis, but not in the direction to perpendicular to [001]. Carboxylic acids accelerated the overall crystal growth and this increase was more enhanced along the c-axis than that along others. Both effects were observed using α-hydroxy acids. In addition, the present results implied that the size of the hydrocarbon groups in alcohols and α-hydroxy acids appeared to be related to the acceleration of crystal growth along the c-axis. Hydroxy groups may reduce the surface energy of the crystal facets perpendicular to the *c*-axis by their adsorption on those facets, resulting in the formation of rod-like crystals with high aspect ratio.

1. Introduction

Functional ability of crystal is strongly related to its morphology. Solution methods including the flux method are suitable for the control of crystal growth. The crystal morphology is strongly affected by reaction conditions such as solvent, flux, pH, and the presence of additives [1,2]. Titania is one of the most important materials due to its high properties and stabilities. The morphological control of the polymorphs such as anatase, rutile and brookite has been extensively studied. Yang et al. synthesized sheet-like anatase particles with a high fraction of {001} by a hydrothermal treatment [3]. It has been reported that the synthesis of anatase crystals with tunable lengths was achieved using an amine solution and a surfactant [4], and spindle-like anatase particles were formed in a gel [5]. Wang et al. synthesized rutile nanorods by the hydrothermal treatment of $TiCl_4$ in an organic medium containing alcohols and acetic acid, and concluded that water generated by the esterification reaction between the carboxy groups in the acetic acid and hydroxy groups in alcohols and the viscosity of the solution played key roles in controlling the morphology of the product [6]. Other researchers have also described the importance of the viscosity of the reaction medium in the control of crystal growth [7,8]. It has also been claimed that the anisotropic growth of titania crystals is governed by not only thermodynamics, but also by the reaction kinetics [9].

To date, we have succeeded in synthesizing titania with controlled structures and morphologies using a hydrothermal treatment of a series of water-soluble titanium complexes employing additives [10–13]. During this research, we found that anisotropically grown rutile titania nanocrystals along the *c*-axis is as formed by the hydrothermal treatment of a glycolato-titanium complex using glycolic acid, which is the simplest α-hydroxy acid (*R*(OH)COOH), as a morphological control agent, and the aspect ratio increases with an increase in the quantity of glycolic acid added [14–16]. On the other hand, there have been reports on the synthesis of rutile titania using alcohols (*R*OH and (HO)*R*'(OH)) and carboxylic acids (*R*COOH) as additives [17]. For example, Wang et al. revealed that rutile rods with a high aspect ratio were formed by a hydrothermal treatment of $TiCl_4$ in the presence of ethylene glycol as an additive, and produced crystals exhibited improved photocatalytic activity [18]. The size of rod-like shaped rutile crystals obtained using carboxylic acids was smaller than those prepared without additives [19].

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To the best of our knowledge, there are no reports on the relationship between hydroxy and carboxy groups as morphological control agents in the crystal growth of rutile-type titania. This is because the single phase of the rutile crystal, which is the most thermodynamically stable phase in titania polymorphs, is difficult to obtain in the presence of some additives [20–22]. Using a hydrothermal treatment of an aqueous solution of a water-soluble titanium complex, single phase of rutile titania crystals have been obtained without careful control of the conditions [14]. However, a detailed mechanism of the progression of the crystal growth in the reaction solution and an effect of functional groups have not been clarified. Even though it is difficult to experimentally investigate crystal growth mechanisms [23,24], schematic experiments provide some clues to their details. Therefore, in this study, we investigated the effect of hydroxy and carboxy groups on the anisotropic growth of rutile titania crystals in a hydrothermal treatment of a water-soluble titanium complex used in previous research [14,15] to attain "real" tailored synthesis of crystals.

2. Experimental section

Single crystals of an ammonium trilactate titanium $(NH_4)_2[Ti(C_3H_4O_3)_3]$ (Fig. S1), which is one of water-soluble titanium complexes, were prepared by recrystallization method [25,26]. Typically, 10 mmol of titanium metal powder (99.9%, Furuuchi Chemical) was dissolved in a mixture containing 20 cm^3 of H_2O_2 (31.0%, Santoku Chemical) and 5 cm^3 of NH_3 (28.0%, Kanto Chemical) aqueous solutions in an ice water bath. Then, 30 mmol of L-lactic acid (85.0%, Wako Pure Chemical) was added to the solution and it was heated on a hot plate at 353 K to eliminate excess H_2O_2 and NH_3 and execute condensation. Transparent, colorless crystals of the ammonium salt of the trilactate titanium complex were formed during the condensation at 353 K. The crystals were collected by suction filtration, and then dissolved in distilled water. After recrystallized three times followed by drying in vacuum at 298 K, the resulting high purity crystals were used as a titanium source. In the next step, 2 mmol of the complex and 4 mmol of an additive were dissolved in distilled water. In this study, three types of additives; α-hydroxy acid (*R*(OH)COOH), alcohol (*R*OH), carboxylic acid (*R*COOH), were chosen for use. Glycolic acid ($R=CH_2$, 98.0%, Kanto Chemical, GA), L-lactic acid ($R=CH–CH_3$, LA) and DL-2-hydroxybutyric acid ($R=CH–CH_2–CH_3$, 95.0%, Tokyo Chemical, HBA) were selected as the α-hydroxy acids. Methanol ($R=CH_3$, 99.8%, Kanto Chemical, MeOH), ethanol ($R=CH_2–CH_3$, 99.5%, Kanto Chemical, EtOH), 1-propanol ($R=CH_2–CH_2–CH_3$, 99.5%, Kanto Chemical, PrOH), and 1-butanol ($R=CH_2–CH_2–CH_2–CH_3$, 99.0%, Kanto Chemical, BuOH) were used as alcoholic additives. For the carboxylic acid, formic ($R=H$, 98.0%, Kanto Chemical, FA) and acetic acids ($R=CH_3$, 99.5%, Kanto Chemical, AA) were chosen. The total volume of the solution was adjusted to 40 cm^3 by adding distilled water and the solution was transferred to Teflon vessel (50 cm^3). Note that all of the prepared solutions were transparent and no precipitate was observed. This indicated that hydrolysis had not occurred before the hydrothermal treatment as opposed to instances that have occurred with conventional titanium sources. The Teflon vessel was sealed in a stainless steel jacket and heated in an oven at 473 K for 2–48 h. The autoclaves were then cooled to room temperature. The resulting precipitate was separated by centrifugation and washed three times with distilled water. The sample was obtained after drying for overnight in an oven at 353 K. Yields were calculated by dividing sample weight after calcination at 1273 K by weight of 2 mmol titania assuming complete transformation of titania in starting solutions to titania.

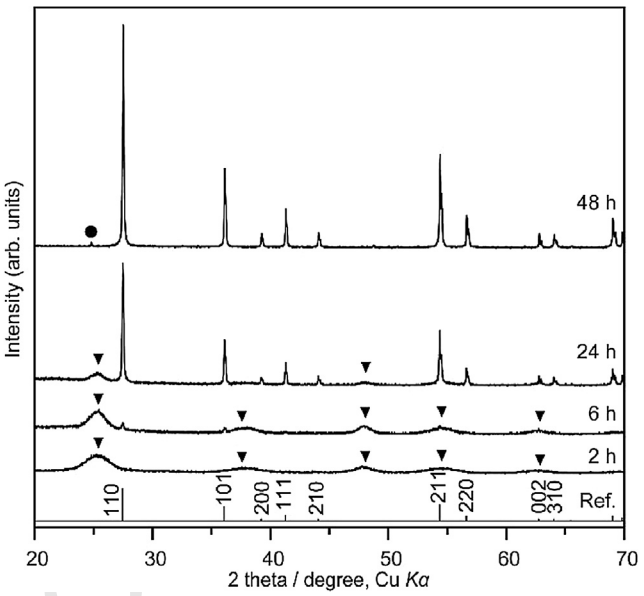

Fig. 1. XRD patterns of samples synthesized by hydrothermal treatment of trilactate titanium complex aqueous solutions at 473 K for (a) 2, (b) 6, (c) 24, and (d) 48 h, triangles and a circle indicate reflections from anatase-type titania and a Kβ peak associated with {110} planes in rutile, respectively. Ref: PDF #78-2485 (rutile, $P4_2/mnm$).

The crystalline phase of the sample was characterized by X-ray diffraction (XRD, Bruker AXS, D2 Phaser) using Cu Kα radiation. To examine the morphologies of the product, transmission electron microscopy (TEM, Hitachi H-7650) was used. Specimens for TEM observation were prepared by sonication of the powders in ethanol followed by placing a drop of the solution on a carbon film-coated copper grid, which was then dried in an oven at 353 K. The average size of the crystals was calculated using 50 randomly selected crystals observed from the TEM images. Selected-area electron diffraction (SAED) patterns and the corresponding TEM images were obtained using another TEM system (Hitachi HF-2000) at an accelerating voltage of 200 kV that was equipped with a double-tilt holder.

3. Results and discussion

3.1. Synthesis of single phase rutile

Hydrothermal synthesis of titania using a trilactate titanium complex has not been reported in detail. Therefore, before investigating the effects of additives on the crystal growth behavior of the rutile crystals, the synthesis conditions of the titania using the described complex were examined. Fig. 1 shows the XRD patterns of the powders obtained by the hydrothermal treatment of the aqueous solutions of the trilactate titanium complex ammonium salt without additives at 473 K for various times. The pH of the solutions was 4.3. After 2 h of treatment, several broad peaks were observed, which were assigned to the anatase-type titania. In the sample synthesized for 6 h, peaks assigned to rutile-type titania were confirmed as a secondary phase. With increase of treatment time, it was found that the peaks associated with the anatase phase decreased, resulting in the formation of single phase rutile after 48 h. The ratio of peak intensities did not dramatically change compared with that of the reference material (PDF#78-2485, $P4_2/mnm$). Fig. 2 shows the TEM images of the corresponding samples shown in Fig. 1. The sample obtained after 2 h of treatment was composed of agglomerates of nanoparticles (Fig. 2(a)). Rod-like particles embedded in the agglomerates of nanoparticles were observed in the samples

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