Hydrothermal Synthesis of Pseudocubic Rutile-Type Titania Particles

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Abstract: The functional properties of materials depend strongly on their morphologies. Here, the hydrothermal synthesis of rutile-type titania crystals with pseudocubic shapes using a water-soluble titanium complex is reported. This approach does not require extra additives or doping. Transmission electron microscopy and selected-area electron diffraction analysis revealed that they exposed high-index facets, such as {121}, and high-energy facets, such as {001}, which do not usually appear in rutile crystal. In terms of the formation of steps and kinks on pseudocubic rutile and coexisting anatase and brookite nanoparticles, the adsorption of nanoparticles might inhibit crystal growth, resulting in the formation of crystals with uncommon shapes exposing high-index and high-energy facets.

Keywords: titania; hydrothermal; morphological control; high-index facet

1. Introduction

Ideally, crystal grows to minimize its surface free energy, and the shape of such crystal is described as an equilibrium shape, which is composed of low-energy and low-index facets [1–3]. Crystals synthesized without any structural directing agent usually have a similar shape to the equilibrium one, and the well-defined structures guarantee their functional abilities. However, high-index and high-energy facets are known to serve as highly active sites. Therefore, the synthesis of crystals with different morphologies from equilibrium shapes is a promising way to develop high-performance devices.

Titania (TiO2) is one of the most extensively studied binary metal oxides, because of its high performances as a catalyst, photocatalyst, and pigment, as well as in dye-sensitized solar cells, photovoltaic cells, and so on. Equilibrium shapes of titania polymorphs, such as anatase, brookite, rutile, and TiO2(B), have also been examined by many researchers [4–8], and the synthesis of titania crystals with high-energy facets—that is, morphologies different from those of the equilibrium shapes—has been achieved [9]. Yang et al. synthesized sheet-like anatase particles with a high fraction (~90%) of {001} having high energy by a hydrothermal treatment using hydrofluoric acid [10,11]. Synthesis of anatase crystals with high-index facets, such as {401}, {301}, and {201}, by solution methods using structural directing agents was also reported [12–14]. Compared with reports on anatase, reports on the synthesis of rutile with high-index facets or a large fraction of high-energy facets are fewer, even though both polymorphs are the main targets of titania research from the early period. Based on the Wulff construction, the equilibrium shape of rutile has been reported as a tetragonal prism bounded by {110}, which is the most stable plane among the rutile crystal facets, and terminated by a pair of
tetragonal pyramids bounded by \{011\} [4–6]. The shape is usually called a “rod”. Most studies about morphological control of rutile are related to changing the aspect ratio of the rod [9,15,16]. In this case, a fraction of the most stable \{110\} increased or decreased with maintaining the rod shape. It was reported that utilization of tantalum doping or a MoO₃ carrier led to formation of rutile crystal with dominant \{001\}, which disappears during crystal growth due to its high energy [17,18]. In these cases, it is difficult to obtain pure titania. Recently, Truong et al. succeeded in the synthesis of rutile crystal exposing \{331\} by a hydrothermal method using picolinic acid as the structural directing agent [19]. The reason why there are fewer reports on the synthesis of rutile crystals with nonequilibrium shapes is that rutile is the most thermodynamically stable phase among the titania polymorphs. Therefore, the synthesis of rutile crystals with non rod-like shape or exposing high index facet is still challenging.

To date, the authors have reported the synthesis and morphological control of titania polymorphs, including anatase, brookite, rutile, and TiO₂(B), by hydrothermal treatment of water-soluble titanium complexes [20–22]. Hydrothermal synthesis is a promising approach to obtain nonequilibrium shaped oxide crystals because synthesis of not only titania [10–12] but also iron [23,24], tin [25], and copper [26] oxides with high-index facets was achieved. Using a glycolato-oxo-peroxo-titanium(IV) complex [27], which is one of the water-soluble titanium complexes, and additives, we have succeeded in the synthesis of urchin-like and flower-like rutile and spindle and square bipyramid-shaped anatase, and control of aspect ratio of rod-like rutile crystals [19–22,27–31]. In this study, pseudocubic rutile composed of large fractions of high-index facets, such as \{121\}, and high-energy facets, such as \{001\}, was successfully synthesized by hydrothermal treatment of the glycolato-oxo-peroxo-titanium(IV) complex, which is one of the water-soluble titanium complexes, without additives.

2. Materials and Methods

Titania was synthesized by hydrothermal treatment of a glycolato-oxo-peroxo-titanium(IV) complex [27]. First, 20 mmol of titanium metal powder (99.9%, Furuuchi Chemical, Tokyo, Japan) was dissolved in a mixture of 40 mL of hydrogen peroxide solution (31.0 w/v%, Santoku Chemical, Tokyo, Japan) and 10 mL of ammonia solution (28.0 w/v%, Kanto Chemical, Tokyo, Japan) in an ice bath under ambient conditions. The titanium powder dissolved completely after 2 h, and a yellow solution of a peroxo-titanium complex formed. Then, 30 mmol of glycolic acid (98.0%, Kanto Chemical, Tokyo, Japan) was added immediately. This solution was heated at 353 K to enhance complexation and to remove excess hydrogen peroxide and ammonia until it turned into an orange gel-like substance. It was dissolved in distilled water to prepare an aqueous solution of the glycolato-oxo-peroxo-titanium(IV) complex ammonium salt (details of the reaction including chemical equations were discussed elsewhere [20,27]). Several batches of the preparation were combined to obtain a stock solution. The concentration was set to 0.25 M as titanium atom by adding distilled water. In the next step, 40 cm³ of titanium solutions with [Ti] = 12.5, 25.0, 50.0, 75.0, and 100 mM was prepared using 2, 4, 8, 12, and 16 cm³ of the stock solution and the corresponding amount of distilled water. The pH of the solutions was 5.7–5.9; therefore, pH is ignored when the formation mechanism of titania depending on titanium concentration is discussed. The solution was transferred to a Teflon vessel (50 cm³). The Teflon vessel was sealed in a stainless steel jacket and heated in an oven at 473 K for 1 to 168 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 overnight in an oven at 353 K. Yields, \((100 \times X/Y)\)% were calculated by dividing collected sample weight, X g, by weight, Y g, of titania assuming complete transformation of titanium in starting solutions to titania. For example, Y is 0.160 using [Ti] = 50 mM.

The crystalline phase of the sample was characterized by X-ray diffraction (XRD, D2 Phaser, Bruker AXS, Karlsruhe, Germany) using Cu Kα radiation. The titania polymorph ratio (rutile:anatase:brookite) and crystalline size were calculated using Topas software (version 4.2, Bruker AXS, Karlsruhe, Germany) based on Rietveld refinement. To examine the morphologies of products, transmission electron microscopy (TEM, H-7650, Hitachi High-Technologies, Tokyo, Japan) and field emission...
scanning microscopy (SEM, S-4800, Hitachi High-Technologies, Tokyo, Japan) were 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. Selected-area electron diffraction (SAED) patterns and the corresponding high-resolution TEM images were obtained at an accelerating voltage of 200 kV using other TEM systems (HF-2000, Hitachi High-Technologies, Tokyo, Japan and JEM-2100F, JEOL, Tokyo, Japan equipped with a double-tilt holder.

3. Results

Figure 1a,b show XRD patterns of samples obtained using aqueous solutions of the glycolato-oxo-peroxo-titanium complex with various titanium concentrations at 473 K for 72 h and with [Ti] = 50 mM at 473 K for various times, respectively. The weight contents, in percent, of the phases are summarized in Figure 1c. At 72 h of treatment, rutile-type titania was formed without any other phases using solutions with [Ti] = 75 and 100 mM. A small amount of anatase and brookite-type titania was present in the predominantly rutile sample synthesized at [Ti] = 50 mM. The amount of rutile formed decreased with a decrease in the concentration of titanium in the starting solutions. Finally, the formation of rutile was not confirmed on the hydrothermal treatment of the solution with [Ti] = 12.5 mM, and a mixture of anatase and brookite was obtained. One-hour treatment using the solution with [Ti] = 50 mM did not lead to formation of titania; instead, a transparent yellow solution, whose appearance was the same before treatment, was confirmed. On 2 h of treatment, anatase was obtained as the main phase in the presence of trace amounts of brookite and rutile. The yield was approximately 60%. With increase of treatment time, the peak intensity corresponding to rutile became strong. This indicates that the content of rutile in samples increases by prolonged treatment, and this was also confirmed by calculation, as shown in Figure 1c. The yield also gradually increased and reached 90% at 72 h of treatment. Considering experimental loss, almost all titanium might transform into titania on 72 h of treatment.

![Figure 1](image)

Figure 2 shows TEM images and the corresponding SAED patterns of the samples shown in Figure 1. The habit of a crystal is illustrated in Figure 2d. Rod-like particles with dimensions of approximately 240 nm x 60 nm were obtained by hydrothermal treatment of the solution with [Ti] = 100 mM at 473 K for 72 h (Figure 2a). The SAED analysis revealed that the long axis of rod-like particles was parallel to the c-axis and terminated by [111], and the major exposed facet was [110]. Such rod-like particles are frequently obtained by the hydrothermal method, and the shape is close.
to the equilibrium shape of rutile-type titania [4–6]. Hydrothermal treatment of aqueous solutions of the glycolato-oxo-peroxo-titanium complex with the titanium concentration of more than 100 mM produced similar rod-like rutile crystals [28,29]. When the solution with [Ti] = 75.0 mM was used, square particles were observed in addition to rod-like particles (Figure 2b). SAED patterns revealed that some of the particles in the sample were twin (Figure 2c). Whereas the SAED pattern of the tip of the crystal indicated that it was single crystal and terminated by {101}, that of the middle was composed of a set of single-crystal spots. These diffractions clearly represent the twin nature (Figure 2d). Particles with approximately 100 to 130 nm square surrounded by nanoparticles with rod and sphere shapes were observed in the sample synthesized at [Ti] = 50.0 and 25.0 mM (Figures 2e,f). A mixture of spherical particles with diameters of approximately 8 nm and rod-like particles with dimensions of approximately 10–20 nm × 8–15 nm were obtained from the solution with [Ti] = 12.5 mM (Figure 2g). Hydrothermal treatment for 2 h produced agglomerations of tiny particles (Figure 2h). When treatment time was prolonged to 12 h, square particles appeared in agglomerations of nanoparticles (Figure 2i). The size of the square particles increased with an increase of treatment time (Figures 2j,k).

Figure 2. (a–c,e–k) Transmission electron microscopy (TEM) photographs and corresponding selected-area electron diffraction (SAED) patterns of titania obtained by hydrothermal treatment of aqueous solutions of the glycolato-oxo-peroxo-titanium(IV) complex at 473 K: (d) schematic illustration of the rutile crystal based on SAED analysis shown in (c) (circles indicate the places where SAED patterns were taken).

Figure 3 shows TEM and SEM images and corresponding SAED patterns of square particles obtained by hydrothermal treatment of the complex aqueous solution with [Ti] = 50 mM for 120 h. SAED analysis indicated that the square particle was rutile-type titania consisting of {110} and {001} (Figure 3a). In other words, the nanoparticles attached on the square ones are anatase and brookite. An SEM image of the same area, as shown in Figure 3a, clarified that the rutile crystal had a cuboid shape, not platelet or sheet (Figure 3b). Steps and kinks were observed at the edge of the cuboid-shaped
rutile crystal by high-resolution TEM analysis (Figure 3c, indicated by red arrows); therefore, the shape of the present rutile crystal is pseudocubic. Rutile crystals with pseudocubic shapes have rarely been reported. The [001] of rutile does not appear at the equilibrium shape because of its high energy, even though it is a low-index facet. In fact, rutile particles synthesized often expose {001}; however, it is quite a small fraction and not a major exposed facet. Nevertheless, pseudocubic rutile-type titania particles with a large fraction of {001} were obtained in the present study. Considering the observation of steps and kinks, it can be said that “grown shape” rutile was formed. The clear lattice fringes shown in Figure 3c also indicate that the obtained nanocrystals have high crystallinity. The TEM and the corresponding SAED images of another pseudocubic particle revealed that some of the rutile crystals were terminated by high-index facets, such as {121} (Figure 3d). This also indicates that the present rutile crystal was under growth.

**Figure 3.** (a,c,d) TEM micrographs with corresponding SAED patterns and (b) an scanning electron microscopy (SEM) photograph of pseudocubic particles obtained by hydrothermal treatment of the aqueous solution of the glycolato-oxo-peroxo-titanium(IV) complex with [Ti] = 50 mM at 473 K for 120 h: the observed areas in (a) and (b) were the same; (c) high-magnification image taken at a dotted square in (a); red arrows and yellow circles indicate step or kink and the places where SAED patterns were taken, respectively.

### 4. Discussion

In the present method, no additives were required for obtaining titania crystals with pseudocubic shapes; one crystal exposed a large fraction of high-energy facets with a low-index, and another exposed high-index facets. In addition, such unusual particles only formed under a suitable titanium concentration, [Ti] = 25–75 mM. Considering the formation of steps and kinks and the coexistence of nanoparticles, a formation mechanism is proposed, as illustrated in Figure 4. During hydrothermal treatment, first, the complex is decomposed, and anatase, brookite, and rutile-type titania nanoparticles are formed as agglomerates ((ii) → (iii)). With the increase of treatment time, the crystalline size of each polymorph and a fraction of the rutile increased, as summarized in Table 1 and Figure 1c. Anatase and brookite do not transform into rutile directly in the present treatment, even though they are thermodynamically metastable and transform into rutile by thermal treatment in air [28]. Thus, dissolved anatase and brookite accelerate rutile growth ((iii) → (iii)). Rutile growth occurs in agglomerates; therefore, anatase and rutile nanoparticles surrounding rutile crystals might inhibit
the crystal growth of rutile, resulting in the formation of pseudocubic crystals with high-index facets or high-energy facets with low-index ((iii) → (iv)). The formation of a twin is another evidence of inhibiting crystal growth. Anatase and brookite did not disappear, even though the treatment time was extended to 168 h (Figure 1c). However, only rod-like rutile crystals, similar to the equilibrium ones, could be obtained as a single phase, when hydrothermal treatment of the complex aqueous solution with [Ti] = 100 mM was performed. Using a solution with the same concentration, anatase:brookite:rutile in the sample synthesized for 12 h was 17.6:2.9:79.5, whereas it was 49.2:28.7:22.1 at [Ti] = 50 mM. That is, to inhibit rutile crystal growth and produce unusual shapes, a large quantity of coexisting nanoparticles led to the formation of nonequilibrium rutile crystals.

![Figure 4. Proposed sequence of pseudocubic rutile crystal formation during hydrothermal treatment of aqueous solution of the glycolato-oxo-peroxo-titanium complex.](image)

Table 1. Particle size of titania polymorphs in samples obtained using the complex solution with [Ti] = 50.0 mM for various treatment times.

<table>
<thead>
<tr>
<th>Treatment Time/h</th>
<th>Crystalline Size/nm</th>
<th>Crystalline Size/nm</th>
<th>Crystalline Size/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Anatase</td>
<td>Brookite</td>
<td>Rutile</td>
</tr>
<tr>
<td>2</td>
<td>4.9</td>
<td>7.7</td>
<td>29.1</td>
</tr>
<tr>
<td>3</td>
<td>5.7</td>
<td>9.7</td>
<td>34.8</td>
</tr>
<tr>
<td>12</td>
<td>8.6</td>
<td>14.0</td>
<td>51.7</td>
</tr>
<tr>
<td>24</td>
<td>10.0</td>
<td>15.6</td>
<td>57.4</td>
</tr>
<tr>
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<td>12.9</td>
<td>19.8</td>
<td>63.7</td>
</tr>
<tr>
<td>168</td>
<td>16.6</td>
<td>23.5</td>
<td>67.2</td>
</tr>
</tbody>
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1 Calculated from XRD patterns using Topas software.

5. Conclusions

Rutile crystals with pseudocubic shapes were synthesized by hydrothermal treatment of a water-soluble titanium complex. The crystals were composed of high-index facets, such as [121], and high-energy facets, such as [001], and their shapes were completely different from the equilibrium one. This is the first report on the synthesis of pseudocubic rutile-type titania crystals without doping and the use of a carrier to the best of the authors’ knowledge. Rutile crystals exposing high-index facets were obtained by changing the titanium concentration in the starting solution. The formation of steps and kinks on pseudocubic rutile crystals indicates that an appropriate number of coexisting anatase and brookite nanoparticles might control the growth of rutile crystals, resulting in the formation of unusually shaped rutile. However, to understand the precise mechanism deeply, the surface energy of
each facet and dynamics of titanium species and water under hydrothermal conditions should also be investigated properly.

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**References**


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