Synthesis of spindle and square bipyramid-shaped anatase-type titanium dioxide crystals by a solvothermal method using ethylenediamine

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Morphological control as well as formation of nanoparticles of anatase-type titanium dioxide has been achieved by a solvothermal treatment of a water-soluble citratoperoxotitanium (CPT) complex using ethylenediamine (EDA) as a key solvent in the presence of a given amount of water. When the EDA concentration in the whole solvent (EDA + H₂O) remained low less than 12 M, the powder obtained after the solvothermal treatment consisted of spindle-like anatase particles. With an increase of the EDA concentration in the solvent, the shape of the obtained particles changed from spindle to square bipyramid. When another water-soluble oxoglycolatoperoxotitanate complex or TiCl₄ was used as a starting source of Ti, similar shaped anatase particles could be obtained by a careful choice of synthetic conditions. Using a mixed solvent of EDA and water, sheet-like titanic acid was produced as an intermediate phase, regardless of the EDA concentration. Therefore, the formation of anatase in the current system may take place through dissolution-recrystallization of titanic acid. The formation of square bipyramidal anatase particle achieved in the present study is not in agreement with a reported theoretical calculation of equilibrium phase, because the calculation reveals that truncated square bipyramid-like anatase is obtained under an acidic condition and spindle-like anatase was formed under a basic condition. An adsorption of EDA on particle surface and the pH of the solvent may contribute to the achievement of morphological control.

Key-words : Solvothermal method, Morphological control, Titanium oxide, Water-soluble titanium complex, Dissolution-recrystallization

1. Introduction
Titanium dioxide (TiO₂) is industrially used in various fields as a pigment, photocatalyst, dielectric substance, and so on. In general, anatase, rutile and brookite-type TiO₂ are the main target of research relating to TiO₂, because the three polymorphs exist in nature and can be easily synthesized. Recently, monoclinic phase TiO₂ [TiO₂(B), bronze-type] has been attracted much attention for its potential ability as a lithium ion battery electrode. In a variety of inorganic materials including TiO₂, it is well-known that their functional ability is strongly dependent on their morphology. Therefore, the establishment of the methodology for morphological control is quite important. To date, we have succeeded in the morphological control of rutile and brookite by a hydrothermal treatment of water-soluble titanium complexes including citratoperoxotitanium (CPT) and glycolatoperoxotitanium (GPT) complexes. However, as to anatase, only nanosized particles could be obtained as long as hydrothermal treatment of the water-soluble titanium complexes is relied on. That’s why a study directed to versatile morphological control of anatase using water-soluble titanium complexes is curious. In the present study, we report on a methodology for synthesis of spindle and square bipyramid-shaped anatase particles, which was achieved by a solvothermal treatment of the CPT using ethylenediamine as a key solvent with varying its concentration. A possible mechanism for the morphological control is also discussed in terms of a dissolution-recrystallization process.

2. Experimental procedure
5 mmol of titanium metal (300 mesh, 99.9%, Furuuchi Chemical) was dissolved in a mixture of 20 cm³ of H₂O₂ and 5 cm³ of NH₃ aqueous solutions in a water bath. After a couple of hours, titanium metal was completely dissolved and a transparent yellow solution of a titanium-peroxo complex was formed. 5 mmol of citric acid was added into the solution and kept it at room temperature for 12 h. To remove an excess amount of H₂O₂ and NH₃, it was heated at 353 K and then yellow gel-like substance was cooled to room temperature, the formed precipitate was separated by centrifuge and washed using distilled water three times. The prepared powder was dried at 353 K prior to further characterization.

XRD measurement of the samples was performed using a RINT 2200 (Rigaku) in a 20–0 scanning mode. Morphology of the powders was observed by scanning and transmission electron microscopy using a S4800 (Hitachi High-tech) and a H7650 (Hitachi High-tech), respectively. For the TEM measurement, the sample was ultrasonically dispersed in ethanol. One drop of the suspension was placed on a carbon coated Cu microgrid and dried at 353 K. Selected area electron diffraction (SAED) pattern and TEM image of anatase particles were taken using a

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high resolution TEM JEM-1200EXII (JEOL) at 200 kV. BET (Brunauer–Emmett–Teller) specific surface areas of the samples were determined by nitrogen adsorption isotherms at 77 K using an ASAP2010 (Micromeritics). Prior to measurement of the surface areas, the samples were degassed at 363 K for 1 h and 473 K for 2 h. FT-IR spectra were recorded on a FT-IR/4200 spectrometer (JASCO) using KBr for dilution (sample/KBr = 1:100).

3. Results and discussion

3.1 Morphological control of anatase-type TiO₂

Figure 1 shows XRD patterns of samples synthesized by the solvothermal treatment of the CPT complex using EDA solutions with various concentrations, CEDA = 0.0 M, 0.7 M, 3.0 M, 7.4 M, 9.7 M, 11.2 M, 12.7 M, and 13.4 M.

A: anatase, B: Brookite, H₂TiO₃O₂-H₂O

Fig. 1. XRD patterns of samples obtained by solvothermal treatment of a CPT complex at 473 K for 24 h in EDA solutions with CEDA = (a) 0.0 M, (b) 0.7 M, (c) 3.0 M, (d) 7.4 M, (e) 9.7 M, (f) 11.2 M, (g) 12.7 M, and (h) 13.4 M.

CPT complex made morphology of produced powders drastically changed in the presence of EDA even at a relatively small concentration. The sample synthesized at CEDA = 0.7 M consisted of anatase and a very small amount of brookite contained approximately 140 x 40 nm² rod-like particles and 80 x 50 nm² rhomboid-shaped particles [Fig. 2 (b)]. In the powder synthesized at CEDA = 7.4 M, snowflake-like agglomerations and ellipsoid-like particles with 750 x 70 nm² were observed [Fig. 2(c)]. The snowflake-like agglomeration could be identified as a brookite, as reported. Ellipsoid-like particles were also formed from solutions at CEDA ranging from 9.7 to 11.2 M [Figs. 2(d) and 2(e)]. The major axis was decreased (750 nm at CEDA = 7.4 M, 320 nm at CEDA = 11.2 M) with an increase of CEDA, while the minor axis remained almost the same (70 nm at CEDA = 7.4 M, 100 nm at CEDA = 11.2 M). As a whole, the size of ellipsoid-shaped particles was decreased with the increase of CEDA. The sample obtained by the solvothermal treatment of the CPT complex at CEDA = 12.7 M, which contained only anatase as a TiO₂, was composed of rhomboid-shaped particles with defined crystal facets [Fig. 2(f)]. Sheet-like tiny particles were adsorbed on the rhomboid-shaped particles. Agglomerations of the sheet-like particles could be observed in the sample synthesized at CEDA = 13.4 M which correspond to H₂TiO₃O₂H₂O. Specific surface areas determined by nitrogen adsorption isotherms were in good agreement with the morphologies observed by TEM, that is, the size order is identical to the specific surface area order.

Figure 3 shows a SAED pattern together with the corresponding TEM image of a given ellipsoid-like particle obtained by the solvothermal treatment of the CPT complex with CEDA = 7.4 M at 473 K for 24 h. The SAED pattern revealed that the ellipsoid-like particle was a single crystal of anatase. Moreover it was clear that the major axis was parallel to c-axis. These results indicate that the morphology of anatase particle can be controlled from a nanoparticle with 10 nm to a spindle-like particle with 700 nm by adjusting CEDA in the current solvothermal system using the EDA/H₂O solution of the CPT complex.

Figure 4 shows SEM images of anatase particles with various morphologies. Shapes of particles obtained at CEDA between 7.4 and 11.2 M were spindle-like, although their aspect ratios and particle sizes were different from each other [Fig. 4(a)–4(c)]. On the other hand, it can be seen that particles synthesized at CEDA = 12.7 M were a single crystal of anatase. Moreover, it was clear that the major axis was parallel to c-axis. These results indicate that the morphology of anatase particle can be controlled from a nanoparticle with 10 nm to a spindle-like particle with 700 nm by adjusting CEDA in the current solvothermal system using the EDA/H₂O solution of the CPT complex.

Figure 5 shows FT-IR spectra of anatase particles obtained by the solvothermal treatment of the CPT complex with CEDA = 0.0 M and 11.2 M at 473 K for 24 h. IR spectrum of a commercial anatase-type TiO₂ (98.5%, Kanto chemical) is also displayed in Fig. 5. When spectra of the obtained anatase were compared with that of the commercial anatase, any extra peaks couldn’t be observed except for a broad peak between 2800–3300 cm⁻¹, which may be arisen from an adsorbed OH group. The result indicates that organic compounds were not adsorbed on the surface of anatase particles synthesized in the current study.

3.2 Speculative formation mechanism of anatase with various morphologies

Figure 6 shows XRD patterns of samples synthesized with CEDA = 11.2 M at 473 K for various solvothermal treatment
A single phase of H$_2$Ti$_2$O$_5$·H$_2$O was obtained without any TiO$_2$ phases [Fig. 6(a)]. On the assumption that the obtained sample is consisted of only crystalline H$_2$Ti$_2$O$_5$·H$_2$O, the observed yield was over 90% according to the TG–DTA measurement. Taking into account a possible sample loss during the synthesis, one can say that all of the complex present in the solution was decomposed and converted into the powder under the solvothermal condition at $t_s = 3$ h. At $t_s = 12$ h, anatase was formed with titanic acid as a secondary phase [Fig. 6(b)]. At $t_s = 24$ and 100 h, single phase of anatase formed [Figs. 6(c) and 6(d)]. Intensity and half maximum full-width of XRD peaks of both the samples synthesized at $t_s = 24$ and 100 h are almost the same. Additionally, from any EDA solutions of the CPT complex, titanic acid was obtained by the solvothermal treatment at $t_s$ shorter than 12 h, except for the hydrothermal treatment without using EDA as a solvent, and anatase was formed at longer $t_s$ than 100 h. Therefore, it can be concluded that H$_2$Ti$_2$O$_5$·H$_2$O was converted into anatase by the

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Fig. 2. TEM images of powders synthesized from solvothermal treatment of CPT complex EDA solutions at 473 K for 24 h. $C_{EDA} =$ (a) 0.0 M, (b) 0.7 M, (c) 7.4 M, (d) 9.7 M, (e) 11.2 M, (f) 12.7 M, and (g) 13.4 M. BET specific surface areas of each sample are shown in the upper right in the corresponding images.

Fig. 3. SAED pattern and TEM image of an ellipsoid-shaped particle obtained by solvothermal treatment of the CPT complex with $C_{EDA} = 7.4$ M at 473 K for 24 h.
solvothermal treatment at 473 K.13,14) TEM photographs of samples obtained by the solvothermal treatment of the CPT complex with $C_{\text{EDA}} = 11.2$ M at 473 K for various times ($t_{st}$) are shown in Fig. 7. Agglomerations consisting of tiny particles were obtained at $t_{st} = 3$ and 12 h [Figs. 7(a) and 7(b)]. Their shapes identified neither as an ellipsoid nor as a rhomboid. The particle sizes of the two samples were almost the same according to the estimation derived from the specific surface areas measurements. From $t_{st} = 100$ h, ellipsoid-shaped particles similar to those obtained at $t_{st} = 24$ h were formed, though the minor axis of ellipsoids obtained at $t_{st} = 100$ h was shorter than those obtained at $t_{st} = 24$ h [Fig. 7(c)]. When the titanic acid obtained by the solvothermal treatment of the CPT complex in EDA solution was hydrothermally re-treated in an aqueous solution at 473 K for 24 h, single phase of anatase was formed. The shape of the obtained anatase was characterized as inhomogeneous rod-like particles, which differs clearly from the shape of anatase particles synthesized by the solvothermal treatment of the CPT complex at 473 K for 24 h.9) According to the results mentioned above, the anatase formation route in the current system using CPT complex in EDA/H$_2$O solution can be described as follows:

![Fig. 4. SEM images of anatase particles obtained by solvothermal treatment of the CPT complex in EDA solution at 473 K for 24 h. $C_{\text{EDA}} =$ (a) 7.4 M, (b) 9.7 M, (c) 11.2 M, (d) 12.7 M.](image)

![Fig. 5. IR spectra of the anatase particles obtained by solvothermal treatment of the CPT complex in EDA solution at 473 K for 24 with $C_{\text{EDA}} =$ (a) 0.0 M, (b) 11.2 M, and of (c) commercial anatase sample (Kanto Chemical).](image)

![Fig. 6. XRD spectra of samples obtained by solvothermal treatment of 11.2 M EDA aqueous solution of the CPT complex at 473 K at $t_{st} =$ (a) 3 h, (b) 12 h, (c) 24 h, and (d) 100 h.](image)

![Fig. 7. TEM images of powders obtained by solvothermal treatment of a CPT complex in EDA solution with $C_{\text{EDA}} = 11.2$ M at 473 K at $t_{st} =$ (a) 3 h, (b) 12 h and (c) 100 h. TEM image of the samples obtained at $t_{st} = 24$ h is shown in Fig. 2(e). BET specific surface areas of each sample were shown in the upper right in the corresponding images.](image)
It seems that the anatase particle shape is regulated by C$_{EDA}$. When TiOCl$_2$, which was prepared from TiCl$_4$, was used as a starting material, irregular shaped titanic acid was produced by a solvothermal treatment with C$_{EDA}$ = 12.7 M at 473 h for 24 h. The treatment at $t_4$ = 48 h caused formation of anatase, which was characterized as irregular rod-like and rhomboid-shaped particles. A precipitate was produced during the course of preparation of the TiOCl$_2$-EDA solution. The precipitate was regarded as a coarse and amorphous titanium hydroxide agglomeration with low solubility at room temperature, and it may cause the subsequent reaction to become inhomogeneous. That’s why the mixture of various shaped particles was obtained when TiOCl$_2$ was used as a source of Ti. On the other hand, using GPT complex, a similar result to the case using CPT complex with respect to the shape control was obtained, though the averaged particle size was a bit smaller than that obtained from the CPT complex. From these results, precise control of anatase particle (nanosize, spindle, and square bipyramid) can be attained by combination of the use of water-soluble titanium complexes and changing of C$_{EDA}$.

A relationship between C$_{EDA}$ and the anatase shape can be summarized as indicated in Fig. 8. The higher the concentration of EDA (C$_{EDA}$) induces the shorter the aspect ratio of the formed anatase particles. It is well-known that an equilibrium shape of anatase is a truncated square bipyramid consisting of {001} and {101}. Additionally, it has been reported that the equilibrium shape changes depending on the environmental condition and that spindle-like construction, which is consisted of {001}, {101}, and {010}, appeared under a basic condition. Sugimoto et al. have succeeded in a synthesis of spindle-like anatase particles by a “gel-sol” method using titanium tetraisopropoxide and amines as additives. The result is in good agreement with the theoretical calculation of equilibrium phase, because their experiment was carried out under a basic condition. In the present research, spindle-like particles, which are similar to the equilibrium shape of anatase predicted by the theoretical calculation under the basic condition, were obtained using the CPT complex with C$_{EDA}$ = 7–11 M. However, at a higher basic condition, that is, at C$_{EDA}$ beyond 12.7 M, square bipyramid-shaped particles were formed. The formation of square bipyramidal particles cannot be explained in terms of the theoretical calculation of equilibrium shape. When spindle-like anatase was obtained, the amount of EDA in the solution was 40 times higher than Ti in the reaction solution. A detailed mechanism remains still is unclear, however, adsorption manner of EDA on the surface of a given particle and the surface characteristics themselves under high basic condition may presumably affect the morphology of anatase to great extent.

4. Conclusions

Spindle and square bipyramid-shaped anatase particles as well as nanosized particles could be synthesized by a solvothermal treatment of CPT complex in EDA solution. High EDA concentration around 12 M caused formation of square bipyramid-shaped anatase particle, while spindle-like anatase was formed from lower EDA solution between 7–11 M. It was confirmed that the obtained anatase was grown along c-axis. H$_2$Ti$_2$O$_5$·H$_2$O was formed as an intermediate phase and the formation of spindle and square bipyramid-shaped particles were followed by dissolution-recrystallization process. The result of the formation of square bipyramid-shaped anatase is not in agreement with the theoretical calculation of equilibrium phase. A further discussion is required to elucidate a detailed mechanism with respect to the morphological control of anatase.

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References


