Morphology of anatase crystals and their aggregates synthesized hydrothermally from aqueous mixtures of titanium alkoxide and different alkylammonium hydroxides

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Anatase was hydrothermally synthesized from transparent aqueous sols including layered titanate colloids. The reaction sols were prepared from titanium isopropoxide and different alkylammonium hydroxides (NR₄OH). The influence of the type of NR₄OH on the morphology of the anatase crystals and their aggregates was examined. We previously reported that although anatase has a tetragonal lattice, six-pointed starlike anatase aggregates were synthesized from the sols prepared using N(CH₃)₄OH. With increasing the alkyl chain length of NR₄OH, the number of the starlike aggregates decreased, and their arms became thicker and shorter. When N(C₄H₉)₄OH was used, needlelike anatase crystals elongated along the c-axis were formed rather than starlike aggregates. The use of NR₄OH with long alkyl chains were expected to retard stacking of the layered titanate during hydrothermal synthesis. The stacking and exfoliation of the layered titanate colloids may play an important role in the morphology of the resulting anatase crystals and their aggregates.

Key-words: Titania, Hydrothermal synthesis, Transparent colloidal solution, Crystal aggregate

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1. Introduction

Bottom-up synthesis process as aqueous solution processes is useful for the synthesis of ceramic nanoparticles and films with interesting nanostructures. For such syntheses, the control of the morphology of nanocrystal building blocks and their assembly can provide complex and hierarchical nanostructures, which lead to superior material properties. In some cases, mesocrystals of nanocrystal building blocks have interesting shapes, which are not deducible from the crystal system of the nanocrystal building blocks. For morphology control of such mesocrystals, it is necessary to know how the building blocks are assembled. Previously, we reported the synthesis of six-pointed starlike anatase aggregates having a six-fold symmetry (Fig. 1), although anatase has a tetragonal lattice. Microstructure analysis of the aggregates, which we synthesized, showed that they consisted of acicular anatase crystals elongated along the c-axis, which were arranged parallel to each other, to form a half of the arm, as shown in Fig. 2. The crystals in both sides of the arms were connected in a twinning way. The twin boundary is {112} planes, and the internal angle between {112} and {112} planes of about 60°, exactly 58.8°, is responsible for the six-fold symmetry of the aggregates. The aggregates were hydrothermally synthesized from transparent colloidal aqueous solutions. The solutions were prepared by mixing Ti(OPrᵢ)₄ and N(CH₃)₄OH, and included layered titanate colloids with a lepidocrocite-type structure. TEM observation of the aggregates suggested that the stacking of the titanate colloids and sequential topotactic structural conversion of the titanate to anatase play an important role in the formation of the acicular anatase crystals, as shown in Fig. 2. If this formation process of the acicular crystals is right, the use of NR₄OH with long alkyl chains instead of N(CH₃)₄OH can influence the morphology of the synthesized crystals and their aggregates, because the intercalation of NR₄OH with long alkyl chains into the interlayer of lepidocrocite-type titanates leads to the exfoliation of the titanate layers. In this study, anatase crystals and their aggregates were hydrothermally synthesized from...
the sols prepared using NR₄OH with different alkyl chain lengths. Based on the influence of the alkyl chain length of NR₄OH on the morphology of the anatase crystals and their aggregates, the formation process of them was examined.

2. Experimental procedure

Reaction sols were prepared as follows: 4 mmol of titanium isopropoxide (TIP) was directly added to aqueous solutions of different tetraalkylammonium hydroxides. 15% N(CH₃)₄OH solution, 20% N(C₂H₅)₄OH solution, 10% N(C₃H₇)₄OH solution, and 10% N(C₄H₉)₄OH solution were used as the aqueous solution of alkylammonium hydroxide. The molar ratio of NR₄OH/TIP was changed from 0.5 to 1.5, and is hereafter denoted as R. The mixtures were stirred at room temperature for 2 h, and then hydrothermally treated at 140°C for 24 h. The resulting precipitates were stirred further for 24 h, they were diluted to 40 mL with distilled water. After the aqueous transparent sols thus obtained were stirred further for 24 h, they were used as a reaction sol. The concentration of the reaction sols was 0.1 mol·Ti L⁻¹. The sols were transferred to a Teflon-lined steel vessel having inner content of about 120 mL, and then hydrothermally treated at 140°C for 24 h. The resulting precipitates were collected by centrifugation, washed with sufficient amount of distilled water, and dried at 110°C overnight. The powder thus obtained was used as a sample.

The samples were characterized by means of XRD, SEM and TEM. XRD measurements were performed using a Rigaku Geigerflex RAD–2R with monochromated Cu Kα radiation. SEM and TEM images were captured using a Hitachi model S–4300 and a Hitachi model H–8100, respectively. The SEM observations were made after the deposition of an osmium layer onto the samples. The samples for TEM observation were prepared by dropping a 2-propanol suspension of a powdery sample onto a Cu grid, and then drying it.

3. Results and discussion

Until now, we reported that transparent aqueous sols including titanate colloids were prepared by mixing TIP, N(CH₃)₄OH, and H₂O at mixing ratio R (= N(CH₃)₄OH/TIP) ≥ 0.4,7) and the titanate colloids had a lepidocrocite-type layered structure.4) At first, the preparation of transparent aqueous sols of titanate colloids by using N(C₂H₅)₄OH, N(C₃H₇)₄OH and N(C₄H₉)₄OH instead of N(CH₃)₄OH, and the crystal structure of the titanate colloids were examined. The aqueous mixtures were prepared at R ≥ 0.5. Regardless of the type of the used NR₄OH, all mixtures became transparent sols. In order to investigate crystal structure of the colloids in the sols, the sols at R = 1.0 were applied onto glass substrates, and after they were dried, XRD measurement was conducted for the films thus obtained. Figure 3 shows the XRD patterns. The patterns featured a layered structure, except for the sample synthesized using N(C₄H₉)₄OH. That is, each sample exhibited two or three peaks, whose d-spacings had a relation of 1:1/2:1/3. The intensity and broadness of the peaks, that is, the size, crystallinity and orientation of the titanate layer were dependent on the type of NR₄OH. The peak intensity of the layered titanate increased in the following order: N(C₃H₇)₄OH < N(C₂H₅)₄OH < N(C₄H₉)₄OH < N(CH₃)₄OH. Since the gel prepared from the sol including N(C₃H₇)₄OH showed no peaks, XRD measurement was also conducted for the suspension prepared by treating hydrothermally the reaction sol at 140°C for 6 h. As shown in Fig. 3(d), the gel film prepared from the suspension showed three sharp peaks with d-spacing of 1.82, 0.91 and 0.61 nm, indicating that the titanate colloids in the sols prepared using N(C₃H₇)₄OH had a layered structure or crystallized to a layered compound during hydrothermal synthesis. Although it is known that the intercalation of N(C₄H₉)₄OH and N(C₃H₇)₄OH into the interlayer of lepidocrocite-type layered titanate leads to exfoliation of the titanate layers,10)11) even the use of N(C₄H₉)₄OH provided transparent aqueous sols of crystalline layered titanate colloids. Next, the dependence of the basal spacing of the layered titanate on the type of NR₄OH was examined. The basal spacing of the layered titanate including N(CH₃)₄⁺, N(C₂H₅)₄⁺, N(C₃H₇)₄⁺, and N(C₄H₉)₄⁺ was 1.71, 1.84, 1.82, and 1.75 nm, respectively. The basal spacing of the titanate was not largely changed with the alkyl chain length of NR₄OH, although it was expected that the basal spacing increases with increasing the alkyl chain length of NR₄OH. The reason why the basal spacing of the titanate was independent on the alkyl chain length of NR₄OH is unclear. The followings might influence it: (1) The alkyl chains of the NR₄OH do not always have an all-trans configuration. (2) Not only NR⁺ ions but also water molecules are present in the interlayer of the titanate. The arrangement of the H₂O molecules in the interlayer might also influence the basal spacing.

![Fig. 3. XRD patterns of the gel films prepared from the sols obtained using (a) N(CH₃)₄OH, (b) N(C₂H₅)₄OH, (c) N(C₃H₇)₄OH, and (e) N(C₄H₉)₄OH, and (d) of the gel film prepared from the suspension obtained by hydrothermally treating the sol, which was prepared using N(C₃H₇)₄OH, at 140°C for 6 h.](image1)

![Fig. 4. XRD patterns of the samples synthesized using (a) N(CH₃)₄OH, (b) N(C₂H₅)₄OH, (c) N(C₃H₇)₄OH and (d) N(C₄H₉)₄OH at R = 1.5.](image2)
The TiO\textsubscript{2} crystals synthesized hydrothermally from the reaction sols were examined. At \( R = 1.0 \), all samples featured anatase, although for the sample using N(CH\textsubscript{3})\textsubscript{4}OH, very slight amount of rutile and brookite coexisted. The yield of the anatase was dependent on the type of NR\textsubscript{4}OH, and was about 65\%, 55\%, 100\% and 100\% for the samples synthesized using N(CH\textsubscript{3})\textsubscript{4}OH, N(C\textsubscript{2}H\textsubscript{5})\textsubscript{4}OH, N(C\textsubscript{3}H\textsubscript{7})\textsubscript{4}OH, and N(C\textsubscript{4}H\textsubscript{9})\textsubscript{4}OH, respectively. Figure 4 shows XRD patterns of the samples synthesized at \( R = 1.5 \). At \( R = 1.5 \), the sample synthesized using N(CH\textsubscript{3})\textsubscript{4}OH was a mixture of anatase and layered titanate, while the ones using N(C\textsubscript{2}H\textsubscript{5})\textsubscript{4}OH and N(C\textsubscript{3}H\textsubscript{7})\textsubscript{4}OH featured anatase, although for the ones using N(C\textsubscript{4}H\textsubscript{9})\textsubscript{4}OH, very slight amount of rutile coexisted. The sample synthesized using N(CH\textsubscript{3})\textsubscript{4}OH was a mixture of anatase, brookite, rutile and layered titanate. Since the peak around \( 2\theta = 25^\circ \) to \( 26^\circ \) in Fig. 4(a) is superposition of the (101) peak of anatase and the (210) and (111) ones of brookite, the amount of anatase was not obvious. Based on the comparison in peak intensity between the peak around \( 2\theta = 25^\circ \) to \( 26^\circ \) and the one around \( 31^\circ \), which is the second strongest peak of brookite, the intensity of the anatase (101) peak was estimated. The peak intensity ratio of anatase (101), brookite (210), and rutile (110) peaks, which are the strongest peak for each phase, was estimated as about 1:0.3:0.05. Also for the sample synthesized using N(CH\textsubscript{3})\textsubscript{4}OH, a main formed phase was anatase. The yield of TiO\textsubscript{2} was about 90\% and 100\% for the samples synthesized using N(C\textsubscript{3}H\textsubscript{7})\textsubscript{4}OH and N(C\textsubscript{4}H\textsubscript{9})\textsubscript{4}OH, respectively. These results indicate that anatase was preferentially formed from these reaction sols, and the use of N(C\textsubscript{2}H\textsubscript{5})\textsubscript{4}OH and N(C\textsubscript{3}H\textsubscript{7})\textsubscript{4}OH led to faster structural conversion of layered titanate to anatase than the one of N(CH\textsubscript{3})\textsubscript{4}OH and N(C\textsubscript{2}H\textsubscript{5})\textsubscript{4}OH. The exfoliation of titanate layers by the intercalation of alkylammonium ions having long alkyl chains may play an important role in the fast structural conversion to anatase. For some samples, the coexistence of rutile and brookite was observed. The reason why rutile and brookite coexisted with anatase is unclear. Since the reaction condition as the concentration and pH of the reaction sols were almost same, the reaction rate might influence formed crystalline phase. Next, the morphology of the synthesized anatase and their aggregates was examined. Figure 5 shows SEM images of the samples synthesized using different NR\textsubscript{4}OH at \( R = 1.0 \). The shapes of the anatase crystals and their aggregates were significantly dependent on the type of NR\textsubscript{4}OH. For the samples synthesized using N(CH\textsubscript{3})\textsubscript{4}OH and N(C\textsubscript{2}H\textsubscript{5})\textsubscript{4}OH, many six-pointed starlike aggregates of anatase crystals were observed. Flower-like aggregates, which consisted of aggregates similar to the arms of the starlike aggregates, were also present. For the sample synthesized using N(C\textsubscript{2}H\textsubscript{5})\textsubscript{4}OH, starlike aggregates, needlelike crystals and agglomerates with indistinct shapes were observed. For the sample synthesized using N(C\textsubscript{3}H\textsubscript{7})\textsubscript{4}OH, many needlelike crystals and indistinct agglomerates were observed. With increasing the alkyl chain length of NR\textsubscript{4}OH, the number of the starlike aggregates decreased and the number of the needlelike crystals increased. Furthermore, the dependence of the morphology of the starlike aggregates on the type of NR\textsubscript{4}OH was investigated by means of TEM observation. Figure 6 shows TEM images of the six-pointed starlike aggregates of anatase crystals observed in each sample. Although there were some types of starlike aggregates with different arm shapes, aggregates with a similar arm shape were compared in Fig. 6. Figures 6(a) and 6(b) show starlike aggregates with spindle-shaped arms in the samples synthesized using N(CH\textsubscript{3})\textsubscript{4}OH and N(C\textsubscript{2}H\textsubscript{5})\textsubscript{4}OH, respectively. The arms of the starlike aggregates synthesized using N(CH\textsubscript{3})\textsubscript{4}OH was a little thinner than those using N(C\textsubscript{3}H\textsubscript{7})\textsubscript{4}OH. The use of N(C\textsubscript{4}H\textsubscript{9})\textsubscript{4}OH and N(C\textsubscript{3}H\textsubscript{7})\textsubscript{4}OH provided much thicker and shorter arms. The shape of the anatase crystals, of which the starlike aggregates consisted, was also dependent on the type of the used NR\textsubscript{4}OH. The anatase crystals synthesized using N(CH\textsubscript{3})\textsubscript{4}OH were acicular. With increasing the alkyl chain length of NR\textsubscript{4}OH, the anatase crystals became thicker and had round tip. The electron diffractions captured from the entire starlike aggregates were the same for all aggregates, indicating that they had the same orientation of anatase crystals. As described in the introduction section, our
previous study suggested that the stacking of layered titanate colloids and the topotactic structural conversion of the titanate to anatase provide acicular anatase crystals, and the twinning and oriented attachment of the acicular anatase crystals lead to the starlike aggregates. Regardless of the type of the used NR4OH, the twinning and oriented attachment of anatase crystals occur in the same way. However, the stacking of the layered titanate colloids may be dependent on the type of NR4OH, resulting in different shapes of the anatase crystals. Thus, the exfoliation of titanate layers with NR4OH having long alkyl chains may play an important role in the morphology of the anatase crystals and their aggregates. The use of NR4OH having long alkyl chains led not only to the change in morphology of anatase crystals and their aggregates, but also to the formation of needlelike anatase crystals rather than starlike aggregates, as shown in Fig. 5. Figure 7 shows HR–TEM image captured for the tip of the needlelike anatase crystal. Lattice fringes were seen at an interval of 0.35 nm. The lattice fringes were assigned to {101} planes. The observation indicates that the needlelike crystals were single crystals elongated along the c-axis. Chemseddine and Moritz\textsuperscript{12)} synthesized similar needlelike crystals from diluted sols of the TIP–N(CH\textsubscript{3})\textsubscript{4}OH system. The dilution of the reaction sols may retard the stacking of the layered titanate colloids.

The influence of the amount of NR\textsubscript{4}OH on the morphology of the anatase was also examined. Figure 8 shows SEM images of the samples synthesized using N(C\textsubscript{2}H\textsubscript{5})\textsubscript{4}OH at R = 0.7 and 1.2. At R = 1.2, many starlike aggregates were observed as well as at R = 1.0 (Fig. 5(b)), while at R = 0.7, needlelike anatase crystals coexisted with starlike aggregates. It is expected that the crystallinity of titanate colloids in the reaction sols increases, with increasing R ratio. Thus, insufficient crystallinity of the layered titanate colloids may also lead to needlelike anatase crystals as shown in Fig. 7.

![Figure 6. TEM images and electron diffraction of the starlike anatase aggregates synthesized using (a) N(CH\textsubscript{3})\textsubscript{4}OH, (b) N(C\textsubscript{2}H\textsubscript{5})\textsubscript{4}OH, (c) N(C\textsubscript{3}H\textsubscript{7})\textsubscript{4}OH, and (d) N(C\textsubscript{4}H\textsubscript{9})\textsubscript{4}OH at R = 1.0.](image)

![Figure 7. HR–TEM image of the tip of the needlelike crystals in the sample synthesized using N(C\textsubscript{4}H\textsubscript{9})\textsubscript{4}OH at R = 1.0.](image)

![Figure 8. SEM images of the samples synthesized using N(C\textsubscript{2}H\textsubscript{5})\textsubscript{4}OH at R = 0.7 (a) and 1.2 (b).](image)
4. Conclusions

We previously reported that although anatase has a tetragonal lattice, six-pointed starlike anatase aggregates were hydrothermally synthesized from layered titanate colloids. In order to examine the formation process of the starlike anatase aggregates, anatase was synthesized from aqueous mixtures of TIP and alkylammonium hydroxides having different alkyl chains. The morphology of the synthesized anatase crystals and the starlike anatase aggregates were dependent of the type of NR4OH, as well as the formation rate of anatase was. The use of NR4OH with long alkyl chains were expected to retard stacking of the layered titanate during hydrothermal synthesis. It was found that the stacking and exfoliation of layered titanate colloids had significant influence on the morphology of the resulting titania. These results will provide important information for morphology control of ceramic nanocrystals and their aggregates synthesized from layered compounds.

References