Synthesis and development of titania with controlled structures

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Aqueous solution processes are environmentally friendly and produce materials with excellent properties. We focus on the synthesis of crystals with controlled nano- and microstructures and the development of new materials using aqueous solution-based methods. Using water-soluble titanium complexes, various additives can be used to control morphology. As a result, titania polymorphs including not only anatase and rutile, but also brookite and TiO2(B) with various morphologies were synthesized. In addition, this approach produced magnetite, exposing high index facets. These crystals with controlled structures showed excellent properties. Moreover, the development of new complexes below 373 K was achieved using aqueous solution methods. Water plays a key role in the controlled synthesis of crystalline structures and morphologies and the development of new materials.

Key-words : Titania, Aqueous solution process, Crystal growth, Magnetite, Hydrothermal, Complex, Titanium

1. Introduction

Considering the synthesis of ceramics through solution methods, water is one of the most useful solvents due to its nontoxicity, low cost and easy handling. Ceramics with excellent performance can be often synthesized using aqueous solution methods. Hydrothermal synthesis, which includes the use of supercritical water, and aqueous solution based sol-gel and precipitation methods are widely used for the synthesis of ceramics with controlled structure. There are some reports on ceramic synthesis by bio-inspired and bio-mimetic processes, which are performed using water as a solvent below 373 K.1) Recently, computational simulation reveals that water not only acts as a solvent, but also has a dynamic effect on crystal formation.2) These results attest to the importance of water in material synthesis.

Some elements, such as titanium, tantalum, and niobium, hydrolyze easily and quickly in aqueous solution. Therefore, conventional raw materials are not suitable for aqueous solution methods. For example, alkoxides are hydrolyzed in water immediately. Chlorides are hydrolyzed under ambient conditions with the formation of HCl fumes. Actually, TiCl4 can be dissolved in ice water to form TiOCl2; however, it is not stable, resulting in the gradual formation of amorphous titanium oxide or hydroxide. Substituting the alkoxy groups in metal alkoxides with glycol is an effective way to stabilize elements that otherwise readily hydrolyze.3),4) Glycol-modified compounds can be mixed with water, though such solutions are also hydrolyzed gradually.

In 2001, Kakihana and coworkers reported the preparation of a tetranuclear complex of titanium coordinated by citric acids using a peroxo titanium complex.5) The pH of the aqueous solution of the complex was approximately 6. The solution did not undergo hydrolysis over a wide range of pH values (0–14) and was stable for long periods. Titanium atoms are chelated by deprotonated carboxy and hydroxy groups in citric acid and peroxo groups. The partial charge model suggests that titanium is stabilized, preventing hydrolysis.6),7) Kakihana and coworkers also demonstrated that α-hydroxy acids such as glycolic and lactic acids act as ligands to form stable titanium complexes.8),9) The authors found that water-soluble titanium complexes can be obtained using ethylenediaminetetraacetic acid (edta) and its derivatives as a ligand.10),11) The technique can be applied to the preparation of water-soluble tantalum, niobium, and bismuth complexes.12) They can also be used for ceramic synthesis by aqueous solution methods.

This review mainly focuses on the application of water-soluble titanium complexes. The introduction of water-soluble titanium complexes simplifies the aqueous synthesis of ceramics containing titanium. In addition, the selective synthesis of titania polymorphs with various morphologies is achieved by hydrothermal treatment of water-soluble titanium complexes. Moreover, novel titanium-organic hybrids can be synthesized through aqueous solution methods employing these titanium complexes. In the present review, the synthesis of magnetite with various morphologies is also introduced using similar approaches to demonstrate the utility of the present method.

2. Hydrothermal synthesis of titania

2.1 Selective synthesis of titania polymorphs

Titania is employed in various applications as a white pigment, photocatalyst and so on, due to its high functionality and chemical stability. There are at least eight polymorphs of titania formed under ambient conditions. Among them, anatase (tetragonal) and rutile (tetragonal) are often used and are main targets of research because they can be easily and selectively synthesized. Recently, there has been an increasing number of reports on brookite (orthorhombic) and TiO2(B) (monoclinic) synthesis and their potential as photocatalysts and electrodes in lithium ion batteries.13),14) Note that TiO2(B) is not another term for brookite-type titania. The (B) is derived from VO2(B), where TiO2(B) has an isostructure to VO2(B), and not a bronze-type structure or any other.15)–17) The structural difference of these four polymorphs can be understood in terms of the arrangement of TiO6 units. A number of shared edges in each structure is two, three, four, five, six, and seven.18)–20) Tactoids containing randomly arranged six-membered rings are present in brookite and rutile.21)–22) In rutile, these tactoids slowly intercalate to form a cone-like structure.23)–24) The (B) structure is characterized by a layered structure with an infinite number of shared edges in each structure.
and five for rutile, brookite, anatase and TiO$_2$(B), respectively. Therefore, an order of density is TiO$_2$(B) (3.64 g cm$^{-3}$) < anatase (3.90 g cm$^{-3}$) < brookite (4.13 g cm$^{-3}$) < rutile (4.27 g cm$^{-3}$). The lowest density of TiO$_2$(B) is related to the highest ability as an anode in lithium ion batteries.$^{[21]}$ It was also reported that a thin film fabricated using TiO$_2$(B) kept its photoinduced hydrophilicity in dark for longer time than that of anatase.$^{[25]}$ Brookite thin film exhibited the highest hydrophilicity under UV irradiation among these polymorphs.$^{[26]}$ Theoretical studies revealed that brookite has a comparable dielectric constant to rutile, which showed the highest dielectric constant in monoxides.$^{[27],[28]}$ Synthesis methods to obtain a single phase of brookite or TiO$_2$(B) are complicated and often need special apparatus. In addition, the synthesis conditions for obtaining a single phase of these two titania polymorphs is narrow, requiring precise control and handling. Therefore, reproducibility is poor. This issue is also an obstacle to the widespread application of such titania polymorphs. However, synthesis of single phase brookite and TiO$_2$(B) are intriguing, because they often show excellent properties as mentioned above. In addition, the insufficient studies imply that these polymorphs can exhibit unique functions, which anatase and rutile don’t have.

Hydrothermal treatment of a titanium complex coordinated by lactic or glycolic acid without additives led to the formation of a single phase of rutile.$^{[29],[30]}$ When low temperature (e.g., <473 K) or short treatment times (e.g., <24 h) were used, anatase was formed as a secondary or single phase.$^{[29]}$ On the other hand, rutile was not formed by hydrothermal treatment of the titanium complex coordinated by citric acid, even though high temperature and long treatment times were applied.$^{[29],[30]}$ A single phase of brookite-type titania were obtained by hydrothermally treating a glycolate titanium complex in a basic solution using ammonia, amines or other bases.$^{[12],[29],[32]}$ Formation of brookite was also confirmed in basic solution using other water-soluble titanium complexes prepared from other α-hydroxy acids. However, in almost all cases, anatase and/or rutile was formed as a secondary phase. On the other hand, a single phase of brookite was formed using a complex coordinated by edta without any additives.$^{[14]}$ When complexes prepared using derivatives of edta were hydrothermally treated without additives, brookite tended to form as the main phase.$^{[15]}$ TiO$_2$(B) was obtained as a single phase from the hydrothermal treatment of a glycolate titanium complex in the presence of the proper amount of sulfuric acid.$^{[33]}$ Introducing a large amount of sulfuric acid produced a single phase of anatase. TiO$_2$(B) was not formed using other inorganic acids such as hydrochloric or nitric acid. The detailed mechanism of the selective synthesis of four different titania polymorphs via the same approach is still unclear. However, it seems that the architecture of the complexes is strongly related to the formation of brookite and TiO$_2$(B).$^{[12],[29],[32]}$ It should be noted that each of the obtained polymorphs showed high photocatalytic activity towards the destruction of NO.$^{[29]}$

### 2.2 Titania crystals with various morphologies

Many reports describe the morphological control of anatase and rutile crystals. On the other hand, the synthesis of other polymorphs with various shapes is still challenging. In conventional approaches, the range of synthetic conditions that produces brookite or TiO$_2$(B) is narrow. This is one reason why the synthesis of these crystals with controlled structures is not yet achieved. Various additives can be used as structure directing agents in the hydrothermal synthesis of titania, where water-soluble titanium complexes are used, due to their high stability. Therefore, the present method has high potential to control the morphologies of titania crystals.

**Figure 1** shows transmission electron microscope (TEM) images and the corresponding selected area electron diffraction (SAED) patterns of brookite crystals produced by the hydrothermal treatment of water-soluble titanium complexes. Rod-like brookite crystals with dimensions of 30 nm × 100 nm were synthesized using a low concentration ammonia solution (<1 M) containing the glycolate titanium complex [Fig. 1(a)].$^{[12],[29],[32]}$ SAED revealed that the long axis of the crystals was parallel to the c-axis and they were bounded by the [210] facets. Rod-like brookite crystals are also obtained by other methods, indicating that the rod is an energetically stable form of brookite, even though a reported calculation shows that the equilibrium form of brookite crystals possess seven different facets.$^{[34]}$ Rod-like brookite with high aspect ratio was formed from aqueous solutions of the citrate titanium complex in highly concentrated ammonia (>10 M) [Fig. 1(b)].$^{[35]}$ The crystals grew anisotropically along the c-axis. The aspect ratio of the crystals increases with increasing ammonia concentration. On the other hand, polyhedral-shaped crystals with a low aspect ratio of ~1 were formed using amines, such as dimethylamine [Fig. 1(c)].$^{[36]}$ The TEM and SAED measurements indicated that the obtained nanocrystals had high crystallinity and that the added amine either retarded, or at least did not promote, crystal growth. These results indicate that basic conditions are not responsible for brookite growth along the c-axis; instead, either the ammonium ion or amines affected the growth habit of the brookite crystal. At the present moment, these morphological control cannot be explained qualitatively. As discussed above, even formation of rod-like brookite obtained in many researches is not supported by theory.$^{[34]}$ Elucidation of the detailed mechanism is under further study.

The present method also enables anatase and rutile to be obtained with controlled structure. For example, spindle- and square bipyramidal-shaped anatase was synthesized using high concentrations of an amine, such as ethylenediamine, even though only the single phase of brookite was formed using low concentrations of amine.$^{[27]}$ Note that solvothermal treatment of titanium complexes in rather concentrated amine solutions (e.g., more than 12 M of ethylenediamine) leads to the formation of spherical mesoporous agglomerations composed of tiny particles of...
H$_2$Ti$_2$O$_5$ intercalated with amine. The formation of spheres might be explained by DLVO theory. On the other hand, using 1,3-diaminopropane, multi-pronged needles of anatase crystals were obtained, as shown in Fig. 2(a). Each needle has many steps, indicating the exposure of high-index facets. Rutile crystals with high-index facets were obtained by hydrothermal treatment of an aqueous solution containing a glycolate titanium complex in the presence of picolinic acid, as shown in Figs. 2(b) and 2(c). Flower-like agglomerations composed of rutile rods were observed. SAED revealed that each branch of the flower-like particles were single crystalline in nature. The SAED pattern also illustrated that rutile crystals grew along the [001]. Considering the nature of rutile growth, the tip of each crystal was terminated by [331], which was composed of periodical (110) terraces and (111) steps.

An adsorption manner of additives on surfaces of a given crystal and the surface characteristics might affect morphologies. That is, the preferential adsorption of additives based on the nature of structures of the additive and crystal surfaces could explain the morphological control. For example, on anatase {101} facet, short distances of bridging-O atoms or Ti–Ti atoms are present. Therefore, a bidentate chelation configuration of small molecules such as ethylenediamine might be suitable. In the synthesis of rutile exposing high-index facets using picolinic acid, picolinic acid ions are considered to preferentially adsorb on {111} of rutile due to the mutual π-stacking of a pyridyl ring as follows. The distance between the aromatic rings is of 0.6–0.7 nm depending on the direction. This space can be properly provided on the {111} facets where the distance of Ti–Ti atoms of 0.546 nm-0.649 nm is the largest among low-index planes of rutile. As a result, {111} facets were partially grown together with {110} facets to form pyramidal shape crystals, resulting in formation of high-index surfaces.

### 2.3 The mechanism of crystal growth control

Crystal growth and formation are not currently fully understood. An accumulation of related knowledge leads to tailored synthesis methodologies for crystal preparation. However, it is difficult to construct a methodology only on the basis of experimental results. In this section, a study of the formation mechanism of anisotropically grown rutile crystals using additives is introduced, based on experimental results and simulation.

The aspect ratio of rutile crystal rods can be controlled using α-hydroxy acid in the hydrothermal synthesis of titania. Hydrothermal treatment of a glycolate titanium complex without any additive led to the formation of rod-like rutile particles with an aspect ratio of 2–3 [Fig. 3(a)]. This rod-like shape is similar to the form at equilibrium. In the presence of an α-hydroxy acid, such as glycolic acid, rod-like rutile crystals with a large aspect ratio were formed [Fig. 3(b)]. The aspect ratio increased with an increase in the quantity of glycolic acid added. High resolution TEM and a fast Fourier-transform analysis revealed that the obtained rutile grew along the c-axis. The {110} facets were perpendicularly oriented to the growth direction, and the tips were terminated by the {111} and {001} facets [Fig. 3(c)]. The exposed facets are the same as those of the equilibrium shape deduced from a Wulff construction. However, the aspect ratio of the rutile crystals synthesized in the presence of glycolic acid was greater than 10, while the equilibrium shape of rutile has the ratio of approximately 2. Therefore, the method provided anisotropic rutile particles with a high area ratio of {110} facets. It is also known that the equilibrium shape varies slightly with the experimental conditions under which the crystals are formed, because the surface energy and tension are dependent on the environment. Under basic conditions, rod-like particles with a higher area ratio of {110} particles than those formed under neutral or acidic conditions are estimated. With an increase in glycolic acid concentration, the pH of the solution decreases, that is, rods with low aspect ratio should be formed in the presence of a large amount of glycolic acid. Therefore, experimental results are not supported by the theory.

A molecular dynamics simulation was conducted to elucidate the conformation and dynamics of a glycolate ion [CH$_2$(OH)-COO$^-$] on the {001} and {110} planes of a rutile crystal. The {001} plane is perpendicular to the growth direction and the area of the {110} plane becomes larger as a result of the anisotropic growth in the presence of glycolic acid. The simulation indicated that for both planes, the conformation and dynamics of the ion were strongly dominated by a layered structure of water on the surface. The simulation suggested that the bond between the ion and the surface was more stable on the {110} plane than on the {001} plane. The simulation also suggested that the most stable conformation of the ion at the surface differed between the planes. The carboxy group of the ion on the {110} plane was preferentially oriented toward the surface.
The present work discusses for the first time simulated and experimental titania crystal growth. The present work implies the importance of the total enthalpy. As a result, the direction of functional groups were different in facets. If the glycolate ion binds to a lattice surface site, the incorporation of Ti or O ions onto that site is hindered, slowing growth rate. Logically, the high dielectric constant of the rutile with high aspect ratio might resulted from the anisotropy of dielectric constant and the tensile strain along \{110\}. These results indicate that the hydrothermal treatment of titanium complexes, combined with the suitable use of additives, forms titania crystals with unusual shapes, which showed improved properties.

3. Magnetite with uncommon facets

Fe$_3$O$_4$ (magnetite) is considered to be one of the most important materials, because it is employed in various fields. Magnetite particles are generally formed in an octahedral shape, as the compound has a face-centered cubic (fcc) structure and the order of stability among its planes is \{111\} > \{100\} > \{110\} > others. Therefore, \{111\} faceted octahedral magnetite particles with sizes of 5 to 170 nm are typically obtained by wet chemical processes in the laboratory. To date, there are no reports on the chemical synthesis of magnetite exposing high-index crystal facets, though those facets exhibit high functionality. In this section, the synthesis of magnetite particles of various shapes is reported. Uncommon facets were exposed due to a hydrothermal method employing organic compounds to control the morphology.

Figure 5 shows scanning electron microscope (SEM) images of the samples obtained through the hydrothermal treatment of aqueous iron solutions in the absence or presence of equimolar organic compounds to Fe. X-ray diffraction (XRD) measurements revealed that the samples possess a single phase of magnetite. As shown in Fig. 5(a), the particles synthesized in the absence of the organic compounds had a quasi-octahedral structure, indicating the presence of \{111\} and \{110\} facets, which is consistent with the results on previous studies. Figure 5(b) shows that for a sample produced in the presence of citric acid, octahedral crystals with \{111\} facets were formed. In contrast, when picolinic acid or pyridine was used as the additive, polyhedral particles with triangular, hexagonal, and pentagonal shapes were obtained, along with a small fraction of quasi-octahedral crystals [Figs. 5(c) and 5(d)]. These particles may have high-index facets, because the facet shapes were not formed from only the \{111\}, \{100\} and \{110\} planes. Figure 6 shows an SEM image and the result of an SEM-electron back scatter diffraction (EBSD) analysis of a sample obtained using an equimolar amount of picolinic acid. On the basis of the energy of each facet, it was concluded that the particle had at least \{111\}, \{110\}, \{311\} and \{331\} facets. Other high-index facets might also be present, as many crystal facets have been observed on other crystals [Fig. 5(c)]. Samples prepared using glycolic acid mainly contained octahedral particles with a small proportion of polyhedral particles [Fig. 5(c)].
the first run. The shape and size of the hydrothermally synthesized magnetite appeared to change after the second polymerization, although the polymerization rates were similar for both samples. The change in shape and size possibly resulted from partial leaching of iron during the polymerization, in a manner similar to that of commercial magnetite. Perhaps new surfaces were created after the leaching which exhibited similar activity to that of the fresh surface. Thus, particular iron species located on special surfaces, edges, or corners produced from the formation of high-index facets would be responsible for the catalytic activity inducing polymerization.

4. Development of novel complexes through aqueous solution methods

As discussed in Section 2, the hydrothermal treatment of titanium complexes, irrespective of the additives, produced titania polymorphs with various morphologies. On the other hand, when a solution with some additives was heated to a value below 373 K, organic-titanium hybrids were formed. In this section, recent achievements in the synthesis and properties of novel complexes are summarized.

Figure 7 shows TEM images of samples obtained by heat treatment of an aqueous solution containing a lactate titanium complex and picolinic acid at 368 K for 4 h. Elemental analysis, XRD, thermogravimetric-differential thermal analysis, and Fourier-transform infrared spectroscopy indicated that the obtained compound was a novel titanium complex with a composition of \([\text{Ti}_2\text{O}_3(\text{C}_4\text{H}_3\text{N}_2\text{COO})_2] \cdot 6\text{H}_2\text{O}\) (1). The indexing of this XRD pattern suggested that the crystal has orthorhombic symmetry. Figure 7(a) shows TEM images of samples obtained by heat treatment of an aqueous solution containing a lactate titanium complex and picolinic acid at 368 K for 4 h. Then, a white precipitate was observed. The XRD pattern of the precipitate could not be assigned to any known compounds. Other analysis indicated that the obtained compound was a new titanium complex coordinated by pyrazine-2-carboxylic acid with a composition of \([\text{Ti}_2\text{O}_3(\text{C}_4\text{H}_3\text{N}_2\text{COO})_2] \cdot 6\text{H}_2\text{O}\) (1). The indexing of this XRD pattern suggested that the crystal has orthorhombic symmetry. Figure 7(b) shows TEM images of a part of (a).

5. Conclusions

In conclusion, this study has demonstrated that the hydrothermal treatment of aqueous solutions containing acid-lactate complexes can produce novel titanium complexes with various morphologies. The addition of picolinic acid to the reaction solutions played a crucial role in the formation of these complexes. The use of this method could provide a new approach for the synthesis of novel organic-titanium hybrids, which could be useful in various applications.
These results indicate that the compound has a gate adsorption property. The higher amount of adsorbed water vapor compared to nitrogen might be due to the higher polarity of water than nitrogen. Solution condensation of compound 1 in N,N-dimethylformamide (DMF) led to the growth of single crystals. The single crystal analysis revealed that the compound was a tetragonal system (P4_2/n) with a composition of Ti_6O_8(C_6H_4N_2COO)_(8-)(C_4H_7NO)_4·4C_3H_7NO·H_2O. Some of DMF bond to titanium and the others exist between hexatitanium clusters. The complex has a reversible structural change upon the adsorption–desorption of DMF. Compound 1 was formed when compound 2 was immersed in water. Note that 2 was not obtained from the lactate titanium complex dissolved in DMF and pyrazine-2-carboxylic acid. Therefore, 1 is indispensable for the synthesis of 2.

The same approach using aqueous solutions can be used to synthesize novel complexes of other cations. To date, novel iron complexes coordinated by nitrogen-containing heterocyclic compounds such as picolinic acid were successfully synthesized. These results indicate that water plays an important role in the development of new complexes.

5. Conclusions

The need to synthesize highly functional materials through environmentally benign processes is growing day by day. High functionality is mainly achieved by developing new materials, and by improving existing materials. In this review, the hydrothermal synthesis of highly functional titania and magnetite with controlled nano- and microstructure are summarized. In addition, the development of new complexes with unique properties by aqueous solution methods is also introduced. Water is one of the most useful solvents in modern materials fabrication, because it is inexpensive, harmless and easy to manipulate. Therefore, the hydrothermal approach described in the present review is regarded as an environmentally-friendly process, which can produce materials with excellent properties. Research on titania has been conducted using water-soluble titanium complexes. A series of researches indicates that the development of new raw materials having unique characteristics leads to new strategies, resulting in new materials with higher performance. These results open a perspective for the design of novel functional materials using water as a medium.

Acknowledgement. The author would like to acknowledge Prof. M. Kakihana and Prof. H. Kato (IMRAM, Tohoku University) for fruitful discussions, and Dr. Nada (AIST) for his contributions to the MD simulations and the related discussions. The author would like to express his appreciation to Prof. S. Sato (WPI-AIMR, Tohoku Univ.) and Prof. H. Nishihara (IMRAM, Tohoku Univ.) for their contributions to the development of new complexes. Dr. T. Miyazaki (Tohoku University) made enormous contributions to the TEM, SAED and EBSD measurements and analysis. This work was supported in part by the Grant-in-Aid for Scientific Research (No. 22107002) on the Innovative Areas: “Fusion Materials” (Area no. 2206) and JSPS KAKENHI Grant-in-Aid for Young Scientists (B) (No. 26870048) from the Japanese Government’s Ministry of Education, Culture, Sports, Science and Technology (MEXT).

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