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Abstract Selective synthesis of titanium dioxide (TiO₂) polymorphs including anatase, rutile, brookite and TiO₂(B) by solvothermal treatment of water-soluble titanium complexes is described with a special focus on their morphological control. The utilization of water-soluble titanium complexes as a raw material allowed us to employ various additives in the synthesis of TiO₂. As a result, the selective synthesis of the polymorphs, as well as diverse morphological control, was achieved.

Keywords TiO₂, Solvothermal Treatment, Water-Soluble Titanium Complex, Morphological Control, Selective Synthesis

1. Introduction

Titanium dioxide (TiO₂) has been used in various fields as white pigments, dielectric materials and photocatalysts, etc. Under ambient conditions, titania exists in eight polymorphs, of which rutile, anatase and brookite are in natural polymorphs and TiO₂(B) (bronze) [1,2], TiO₂(H) (hollandite) [3] and the other three polymorphs [4-6] can only be obtained synthetically in the laboratory. Anatase and rutile have wide practical applications, because they can be easily synthesized. On the other hand, there are only a limited number of methods for the single-phase synthesis of the other polymorphs, including brookite [7-16] and TiO₂(B) [1, 2, 17, 18]. Consequently, their functional abilities have not been precisely examined, though they are believed to have high potential as functional materials [19]. Therefore, the development of a method to selectively synthesize rutile, anatase, brookite and TiO₂(B) polymorphs is important.

The functional properties of titania as well as other materials are strongly dependent on its morphology. In general in the inorganic material field, particles show two main types of morphology. The first is the shape of the primary particle, which can be regarded as a single crystal; the second refers to the shape of the secondary particle, which is an agglomeration of primary particles.
Some examples of the secondary particle shape include hollow, porous and solid spheres. The agglomeration of titania showed additional functional abilities such as high absorption rate [20], photonic character [21] and incorporation of organic compounds, gases and ions [22-24]. The primary particles show four types of structures: zero-, one-, two- and three-dimensional structures. Nanosized particles are generally categorized as zero-dimensional structures. Whisker- and needle-like particles are examples of one-dimensional structures; sheet-like particles are examples of two-dimensional materials and the rest are classified as three-dimensional structures.

For evaluating the morphological control of a primary particle, it is important to know which of its facets are exposed, as well as the area ratio of the exposed crystal facets; this is because each crystal facet exhibits different properties. To control which crystal facets are exposed, the equilibrium shape of each polymorph should be understood by taking the Wulff construction [25-27] into account. The equilibrium shape of anatase has been reported as a truncated bipyramidal shape constructed by eight {101} and two {001} (Fig. 1(c)) [28-30].

**Figure 1.** Morphology predicted for anatase (top) with (a) hydrogenated surfaces; (b) with hydrogen-rich surface adsorbates; (c) hydrated surfaces; (d) hydrogen-poor adsorbates; (e) oxygenated surfaces and rutile (bottom) with (f) hydrogenated surfaces; (g) with hydrogen rich surface adsorbates; (h) hydrated surfaces; (i) hydrogen-poor adsorbates; (j) oxygenated surfaces (Reprinted with permission from Reference 30. Copyright 2005 American Chemical Society).

A tetragonal prism bounded by {110} and terminated by a pair of tetragonal pyramids bounded by {011} was the equilibrium shape of rutile when considered for the Wulff construction. The most stable plane among the rutile crystal facets was {110} (Fig. 1(h)) [28-30]. The equilibrium crystal of brookite possessed seven different facets (Fig. 2) [31]. A flat pseudohexagonal prism constructed from {001}, {100}, {110} and {1 10} is the equilibrium shape of TiO2(B) (Fig. 3) [32].

It is also known that the equilibrium shape varies slightly according to conditions under which the crystals are formed, because the surface energy and tension are dependent on environment [30, 33-36]. For example, under basic conditions, rod-like particles surrounded by {101}, {001} and {010} is the equilibrium shape of anatase, while decahedral shape is described from the Wulff construction without any adsorbates (Fig. 1).

A number of studies report that each crystal facet shows different properties [37, 38]. Nakajima et al. [39] evaluated superhydrophilicity on {110} and {001} of rutile single crystals under UV irradiation and found that the hydrophilicity rate on {001} was faster than that on {110}. It was also reported that when the measurement was repeated, the superhydrophilic property on {001} increased, while that on {110} decreased. Ohno et al. [40] concluded that the photocatalytic oxidation and reduction sites of rutile were present on {011} and {110}, respectively. They also found that the oxidation site of anatase was mainly present on {001} and that {011} was more reductive than {001}. However, Kawahara and co-workers reported low activity on the {110} of rutile for the photocatalytic Ag reduction [41]. Moreover, not only empirical results, but also theoretical calculations indicated the differences in the properties of each crystal facet. Based on density functional theory (DFT) and first-principles molecular dynamics simulations, Gong et al. reported that anatase {101} had higher dissociation-adsorption activity for water and ethanol than that of {001} [42]. Based on a modified DFT calculation, Li and co-workers revealed that water and formic acid were adsorbed on each facet of titania in different modes [43].

Some studies have reported the improvement and control of the functional ability of titania by synthesizing titania particles with different morphologies from the particles.
with equilibrium shapes via chemical synthesis methods. Yang et al. [44, 45] synthesized anatase single crystal dominated by {001}, which has higher energy than {011}. As a result, the obtained anatase with the anisotropic shape had a sheet-like nature and showed higher photocatalytic activity than that of anatase with equilibrium shape. Similar anisotropic anatase crystals were obtained by other research groups, who also found that the anisotropic anatase exhibited high photocatalytic activity [46, 47]. Amano et al. synthesized octahedral bipyramid-shaped anatase terminated by {101} with less area of {001} and implied that {011} showed low photocatalytic activity for hydrogen evolution without oxygen [48]. Kanie and Sugimoto fabricated a liquid crystal using c-axis-oriented anatase in combination with organic compounds. Their findings showed that the formation of a liquid crystal was dependent on the degree of crystal anisotropy [49]. These results indicate that developing a methodology for enabling the synthesis of well-faceted and anisotropic titania particles is important for making titania more attractive as a functional material.

Conventionally, in the synthesis of titania, toxic solvents such as HCl (aq.), H2SO4 (aq.) and organic solvents are required, because TiCl4, TiCl3, Ti(SO4)2; and titanium alkoxide are the commonly used titanium sources. In order to meet the rising demand for environmental protection, water should be used as a solvent. However, because the conventional titanium sources are sensitive to water and thus moisture, it is not easy to use water as a solvent in this case. In addition, when using the conventional titanium sources, additives that can work as a morphological control agent are difficult to employ. In 2001, Kakihana et al. developed an ammonium citratoperoxotitanate, (NH4)8[Ti4(CH4O7)4(O2)4]·8H2O [50]. The compound can be readily dissolved in neutral water and the pH of the prepared aqueous solution is approximately 5.6. Moreover, it is stable for up to several years under ambient conditions as a solid and as an aqueous solution, and its ligand (citric acid) is only slightly toxic. In addition, the complex does not undergo hydrolysis in a wide range of pH values (0-14), allowing for the use of various additives. It has been shown that various compounds such as hydroxyacarboclyclic acid, amino acid and amine can be used as ligands to prepare a stable water-soluble titanium complex [51-57].

The authors believe that the water-soluble titanium complex is one of the valuable raw materials for the synthesis of titania with controlled crystal- and microstructures. We have succeeded in selectively synthesizing titania polymorphs, including anatase, rutile, brookite and TiOx(B) by hydrothermal treatment of water-soluble titanium complexes using additives [52, 54, 55, 57-60]. By adjusting the synthesis conditions, the single phase of each titania polymorph can be obtained. In addition, the morphological control of titania crystals was achieved. The reason for achieving selective synthesis might be related to the individual intrinsic characteristics of a series of water-soluble titanium complexes.

In this paper, we summarize our results on the morphological control of anatase, rutile, brookite and TiOx(B) by hydrothermal and in part solvothermal treatment of water-soluble titanium complexes using additives. On the other hand, we do not deal here with details and discussion of selective synthesis of polymorphs, because the points have been already mentioned in a previous paper [55].

2. General Synthesis Procedure

2.1 Preparation of water-soluble titanium complexes

Water-soluble titanium complexes can be prepared from the titanium-peroxo complex [61] and the appropriate ligands. There are many methods for the preparation of the titanium-peroxo complex [62, 63]. Here, we briefly describe the typical preparation procedure used by our group [55]. Titanium metal powder (5 mmol) was dissolved in a mixture of 30.0 % hydrogen peroxide (20 cm3) and 28.0 % ammonia (5 cm3) in a water bath at room temperature. After two hours, a yellow transparent solution containing the titanium-peroxo complex was obtained. A complexant such as glycolic acid or citric acid was added to the solution. The amount of ligand required was dependent on the compound used, which is described in detail elsewhere [55, 57]. To remove excess hydrogen peroxide and ammonia, the prepared solution was left at room temperature for 12 h and then heated at 353 K until a gel-like solid substance was formed. The gel was dissolved in distilled water and an aqueous solution of a titanium complex was then obtained.

2.2 Hydrothermal synthesis of titania nanocrystals

The prepared aqueous solution of a water-soluble titanium complex was heated in a Teflon-lined stainless steel autoclave at a given temperature for a specified amount of time. After the autoclave was cooled to room temperature, the precipitate was separated using a centrifuge and was washed with distilled water three times. The final product was obtained after drying. In this paper, unless stated otherwise, the titanium concentration of the treated solution was 0.25 mol dm-3.

3. Results and Discussion

3.1 Morphological control of rutile-type titania nanocrystals

Single-phase rutile titania powder was obtained by the hydrothermal treatment of a titanium complex prepared using glycolic acid (titanium-glycolato complex) at 473 K for 24 h [52]. The resulting powder consisted of 50 × 150 nm2 rod-like particles (Fig. 4(a)).
The shape is similar to the equilibrium shape of rutile [28-30]. When the treatment time was extended to 100 h, the crystalline phase, size and shape of the particles were maintained (Fig. 4(b)). However, the hydrothermal treatment at 473 K for 6 h produced anatase in the secondary phase. The transmission electron microscopy (TEM) image shows that anatase particles (5 nm) attached to rod-like rutile particles (40 × 120 nm²) were obtained (Fig. 4(c)). These results indicate that the growth of rutile particles in the present system followed the Ostwald ripening law, i.e., dissolution of nano-sized anatase and subsequent recrystallization as the rutile polymorph [64]. Elongated rod-like rutile particles could be synthesized using glycolic acid as an additive in the hydrothermal treatment of the titanium-glycolato complex aqueous solution. The aspect ratio of the obtained rutile particles increased dramatically with an increase in the additional amount of glycolic acid (Fig. 5).

High resolution TEM and selected area electron diffraction (SAED) analysis revealed that the obtained rutile grew along the c-axis; facets that are perpendicular to the growth direction are (110) and the tips terminated by (111) [64, 65]. The exposed facets are the same as those of the equilibrium shape deduced from Wulff construction [28-30]. However, the aspect ratio of rutile crystals synthesized in the presence of glycolic acid was greater than 10, while that of the equilibrium shape of rutile was approximately 2. Therefore, the method provided us anisotropic rutile particles with a high area ratio of [110]. The anisotropic growth of rutile might be caused by selective adsorption of glycolic acid on [110] [29, 33]. Facets chelated with glycolic acid had a lower surface energy than those of bare surfaces. In order to reduce the total energy of the particles, the chelated surfaces were predominantly developed during further particle growth. At the same time, titanium ions were difficult to adsorb on the chelated facets and were therefore preferentially adsorbed on the non-chelated facets (the capping effect). As a result, the obtained rutile particles had a high aspect ratio and the lowest possible fraction of nonchelated facets. When the pH of the titanium-glycolato complex aqueous solution containing excess glycolic acid as the additive was adjusted from approximately ~3 to 5-8 by the addition of ammonia, the formation of the whisker-like particles was prevented, resulting in the formation of the usual rod-like rutile particles. The isoelectric point of TiO₂ has been reported as pH 4.7–6.7 [66-68], which means that the surface of the rutile particles had a negative charge at pH 5-8. Consequently, glycolic acid anions cannot be adsorbed effectively on the rutile surface and hence, cannot promote whisker growth.

Figure 4. TEM images of the rutile particles synthesized by hydrothermal treatment of titanium-glycolato complex without additives at 473 K for (a) 24 h (b) 100 h and (c) 6 h.

Figure 5. TEM images of the rutile particles synthesized by hydrothermal treatment of titanium-glycolato complex in the presence of (a) 5 mmol; (b) 10 mmol; (c) 15 mmol and (d) 25 mmol of glycolic acid as additives at 473 K for 100 h.

Figure 6. TEM images of rutile particles synthesized by hydrothermal method at 473 K for 24 h using titanium-glycolato complex in the presence of (a) lactic acid and (b) oxalic acid with ammonia at pH 3.3.
When lactic acid was added to an aqueous solution of titanium-glycolato complex as the additive instead of glycolic acid, rod-like rutile nanocrystals with a high aspect ratio compared to that of the equilibrium shaped rutile were obtained (Fig. 6(a)). When oxalic acid was used as an additive, the solution pH became less than 1 and single-phase anatase was formed. Using ammonia to adjust the pH to ~3, single-phase rutile was obtained from the solution employing oxalic acid as the additive. However, these rutile particles were rod-like with low aspect ratio and rounded ends (Fig. 6(b)). The reason why rutile particles with a high aspect ratio were not formed might be the high chelating ability of oxalic acid. Oxalic acid can be adsorbed on every facet. As a result, anisotropic growth was not promoted. It is important to note that the hydrothermal treatment of the titanium complex coordinated with leucic acid led to the formation of whisker-like particles with a much higher aspect ratio [57]. This indicates that the aspect ratio of the rutile crystals formed can be controlled by the length of the carbon chain in the hydroxycarboxylic acid used as an additive, though further examination should be performed. We also found that the rutile obtained with a high aspect ratio showed high photocatalytic activity and a robust dielectric constant [65, 69]. These results indicate that the hydrothermal treatment of titanium complexes combined with suitable additives forms anisotropic rutile particles, which showed improved properties.

3.2 Morphological control of anatase-type titania nanocrystals

In general, anatase-type titania can be synthesized as nanosized crystals by solution methods without post-firing. The reason for the formation of nano-sized anatase crystals might be explained in terms of the critical size of titania polymorphs [70]. Anatase nanocrystals can also be obtained by the hydrothermal treatment of water-soluble titanium complexes. Moreover, synthesis of spindle-shaped and square bipyramid-shaped anatase particles has been achieved via a solvothermal treatment using ethylenediamine (en) as a key solvent in the presence of a given amount of water. The hydrothermal treatment of a citratoperoxotitanate (titanium-citrato) complex in distilled water without en at 473 K for 24 h led to the formation of an agglomerate of 10-nm-sized anatase nanocrystals (Fig. 7(a)). When the en concentration in the en/H2O solvent was low, i.e., less than ~75.0 wt%, the powder obtained after the solvothermal treatment consisted of spindle-shaped anatase particles (Fig. 7(b)). A SAED pattern of a spindle-shaped particle revealed that the major axis was parallel to the c-axis [71]. By increasing the en concentration in the solvent, the shape of the particles changed from spindle to square bipyramid (Fig. 7(c)).

These results indicate that the morphology of anatase particles can be modified from a nanoparticle to spindle-shaped by adjusting the concentration of en used in the solvothermal system using the en/H2O solution of the titanium-citrato complex. When the titanium-glycolato complex, or TiOCl₂ (which can be prepared from TiCl₄ and ice water) was used as initial titanium source, anatase particles with a similar shape could be obtained by carefully choosing the synthetic conditions [71]. Using a mixed en/H₂O solvent, sheet-like titanic acid was produced in an intermediate phase, regardless of the en concentration. Therefore, the formation of anatase in the present system may occur through the dissolution-recrystallization of titanic acid. Theoretical calculations revealed that while truncated square bipyramid-shaped anatase should be generated under acidic conditions, spindle-shaped anatase was expected under basic conditions [33, 35]. Nevertheless, square bipyramid-shaped anatase nanocrystals were obtained under relatively high basic conditions used in the present study. Therefore, both the adsorption of en on the particle surface and the solvent pH may contribute to achieving the morphological control of anatase nanocrystals.

3.3 Morphological control of brookite-type titania nanocrystals

As mentioned in the introduction, the synthesis of brookite as a single phase is relatively difficult compared with the synthesis of single-phase anatase and rutile. Therefore, the morphological control of brookite is challenging. In fact, there are only a few reports on the morphological control of brookite particles [13-16]. By hydrothermal treatment of the water-soluble titanium complex, high-quality single-phase brookite particles can be easily synthesized with good reproducibility, as described below. When an ammonia solution was utilized...
as an additive in the hydrothermal treatment of the titanium-glycolato complex at 473 K for 24 h, rod-like brookite nanocrystals, with dimensions of 20 × 50 nm², were formed (Fig. 8(a)).

The size of the obtained brookite particles increased with an increase in the concentration of ammonia in the solvent, while other conditions such as treatment time remained the same. As a result, 80 × 250 nm² rod-like brookite particles were synthesized from a 28.0 wt% ammonia aqueous solution (Fig. 8(b)). The results show that changing the concentration of ammonia in the solvent can control the size of the brookite generated.

When the titanium-citrato complex was used as a titanium source instead of the titanium-glycolato complex, brookite particles with aspect ratios higher than 10 were obtained. Hydrothermal treatment of the titanium-citrato complex in a 28.0 wt% ammonia solution resulted in the formation of 150 × 2180 nm² rod-like brookite particles (Fig. 9(a)). The TEM and SAED measurements provided evidence that growth of the brookite particles occurred along the c-axis [72]. The equilibrium shape of brookite is a polyhedral construction [31]. Therefore, the present brookite particle was an anisotropically grown crystal along the c-axis. At high ammonium concentration, agglomerated brookite particles with unusual shapes, where many rod-like particles were branched around a somewhat longer central particle, also appeared (Fig. 9(b)). The side view of the agglomerated particles revealed two-dimensional crystal growth within a given restricted plane (Fig. 9(c)). The multineedle agglomerate of brookite particles was snowflake shaped and could not be obtained using the titanium-glycolato complex. Brookite with this unique morphology was likely formed because of the intrinsic characteristics of the titanium-citrato complex itself, although the mechanism still remains unclear.

When a suitable amount of amine such as dimethylamine was used as an additive in the hydrothermal treatment of titanium-glycolato complex at 473 K for 24 h, single-phase brookite samples were obtained. The resulting powder consisted of nanocrystals with a low aspect ratio of ~1 (Fig. 10(a)).

When other amines such as monomethylamine and trimethylamine were used as additives, the same effect, i.e., formation of brookite with a low aspect ratio, was observed. The Scanning Electron Microscopy (SEM) measurement revealed that the resulting brookite nanocrystals were polyhedral (Fig. 10(b)). Recently, synthesis of pseudo-cube-shaped brookite nanocrystals by hydrothermal treatment of the titanium-glycolato complex in the presence of oleate salt was reported [73]. The shape of the brookite particles formed was similar to those synthesized by the present method, except for the number of exposed facets. The TEM and SAED measurements indicated that the obtained nanocrystal had high crystallinity and that the added amine either retarded, or, at the minimum, did not promote crystal growth along the c-axis (Fig. 11). These results would indicate that the basic conditions of the solvents were not related to growth along the c-axis; instead, ammonium ion and amine crystal affected the growth habit of the brookite crystal.
3.4 Synthesis of TiO\(_2\)(B) nanocrystals

In 1998, Kasuga et al. reported the synthesis of TiO\(_2\)(B) nanotubes via a multistep method [17, 18]. To date, almost all of the reported methods for the synthesis of TiO\(_2\)(B) have been based on the methods developed by Kasuga et al. We have succeeded in the direct (one-step) synthesis of TiO\(_2\)(B) nanoparticles by the hydrothermal treatment of titanium-glycolato complex in the presence of H\(_2\)SO\(_4\) (Fig. 12) [58].

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6. References

[1] Marchand R, Brohan L, Tournoux M (1980) TiO\(_2\)(B) a new form of titanium dioxide and the potassium octatitanate K\(_2\)Ti\(_8\)O\(_{17}\). Mat. Res. Bull. 15: 1129-1133.
[2] Feist T P, Davies P K (1992) The soft chemical synthesis of TiO\(_2\)(B) form layered titanates. J. Solid State Chem. 101: 275-295.
[3] Latroche M, Brohan L, Marchand R, Touranoux M (1989) New Hollandite Oxide: TiO\(_2\)(H) and K\(_{0.06}\)TiO\(_2\). J. Solid State Chem. 81: 78-82.
[4] Simons P Y, Dachille F (1967) The structure of TiO\(_2\)(II), a high-pressure phase of TiO\(_2\). Acta Crystallogr. 23: 334-336.
[5] Akimoto J, Gotoh Y, Oosawa Y, Nonose N, Kumagai T, Aoki K, Takei H (1994) Topotactic Oxidation of Ramsdellite-Type Li\(_{0.5}\)TiO\(_2\), a New Polymorph of Titanium Dioxide: TiO\(_2\)(R). J. Solid State Chem. 113: 27-36.
[6] Takahashi Y, Kijima N, Akimoto J (2006) Synthesis, Structural Change upon Heating, and Electronic Structure of Ramsdellite-Type TiO\(_2\). Chem. Mater. 18: 748-752.
[7] Ohtani B, Handa J, Nishimoto S, Kagiya T (1985) Highly Active Semiconductor Photocatalyst: Extra-Fine Crystalline of Brookite TiO₂ for Redox Reaction in Aqueous Propan-2-ol and/or Silver Sulfate Solution. Chem. Phys. Lett. 120: 292-294.

[8] Kominami H, Kohno M, Kera Y (2000) Synthesis of brookite-type titanium oxide nano-crystals in organic media. J. Mater. Chem. 10: 1151-1156.

[9] Potter A, Chnéac C, Trone E, Mazerolles L, Jolivet J P (2001) Synthesis of brookite TiO₂ nanoparticles by thermolysis of TiCl₄ on strongly acidic aqueous media. J. Mater. Chem. 11: 1116-1121.

[10] Tang J, Redl F, Zhu Y, Siegrist T, Brus L E, Steigerwald M L (2005) An Organometallic Synthesis of TiO₂ Nanoparticles. Nano Lett. 5: 543-548.

[11] Reyes-Coronado D, Rodrigues-Gattorno G, Espinosa-Pesqueira M E, Cab C, Coss R D, Oskam G (2008) Phase-pure TiO₂ nanoparticles: anatase, brookite and rutile. Nanotechnol. 19: 145605-145614.

[12] Kandiel T A, Feldhoff A, Robben L, Dillert R, Bahnemann S W (2010) Tailored Titanium Dioxide Nanomaterials: Anatase Nanoparticles and Brookite Nanorods as Highly Active Photocatalysts. Chem. Mater. 22: 2050-2060.

[13] Li J G, Tang C, Li D, Haneda H, Ishigaki T (2004) Monodispersed Spherical Particles of Brookite-Type TiO₂: Synthesis, Characterization, and Photocatalytic Property. J. Am. Ceram. Soc. 87: 1358-1361.

[14] Buonsanti R, Grillo V, Carlino E, Giannini C, Kipp T, Cingolani R, Cozzoli P D (2008) Nonhydrolytic Synthesis of High-Quality Anisotropically Shaped Brookite TiO₂ Nanocrystals. J. Am. Chem. Soc. 130: 11223-11233.

[15] Zhao B, Chen F, Huang Q, Zhang J (2009) Brookite TiO₂ nanoflowers. Chem. Comm. 5115-5117.

[16] Hu W, Li L, Tang C, Sun L. (2009) High-Quality Brookite TiO₂ Flowers: Synthesis, Characterization, and Dielectric Performance. Cryst. Growth Des. 9: 3676-3682.

[17] Kasuga T, Hiramatsu M, Hoson A, Sekino T, Niihara K (1998) Formation of Titanium Oxide Nanotube. Langmuir, 14: 3160-3163.

[18] Kasuga T, Hiramatsu M, Hoson A, Sekino T, Niihara K (1999) Titania Nanotubes Prepared by Chemical Processing. Adv. Mater. 11: 1307-1311.

[19] Mo S D, Ching W Y (1995) Electronic and optical properties of three phases of titanium dioxide: Rutile, anatase, and brookite. Phys. Rev. B 51: 13023-13032.

[20] Yoshitake H, Sugihara T, Tatsumi T (2002) Preparation of Wormhole-like Mesoporous TiO₃ with an Extremely Large Surface Area and Stabilization of its Surface by Chemical Vapor Deposition. Chem. Mater. 14: 1023-1029.

[21] Waterhouse G I N, Waterland M R (2007) Opal and inverse opal photonic crystals: Fabrication and characterization. Polyhedron, 26: 356-368.

[22] Hu X, Zhang T, Lin Z, Huang A, Fang M, Wu Y, Zhang L (2009) Single-Crystalline Anatase TiO₂ Dous Assembled Micro-Sphere and Their Photocatalytic Activity. Cryst. Growth Des. 9: 2324-2328.

[23] Lim S H, Luo J, Zhong Z, Ji W, Kín J (2005) Room-Temperature Hydrogen Uptake by TiO₂ Nanotubes. Inorg. Chem. 44: 4124-4126.

[24] Armstrong A R, Armstrong G, Canales J, Bruce P G (2004) TiO₂-B Nanowires. Angew. Chem. Int. Ed. 43: 2286-2288.

[25] Wulff G (1901) Zur Frage der Geschwindigkeit des Wachstums und der Auflösung der Kristallflächen. Ztschr. Krystallogr. Mineral. 34: 449-530.

[26] Herring C (1951) Some Theorems on the Free Energies of Crystal Surfaces. Phys. Rev. 82: 87-93.

[27] Dobruschin R L, Kotecký R, Shlosman S B (1992) Wulff Construction: A Global Shape from Local Interaction. USA: The American Mathematical Society. 204p.

[28] Lazzeri M, Vittadini, Selloni A (2001) Structure and energetics of stoichiometric TiO₂: anatase surfaces. Phys. Rev. B 63: 155409.

[29] Oliver P M, Watson G W, Kelsey E T, Parker S C, Armstrong A R, Armstrong G, Canales J, Bruce P G (2001) Synthesis of Brookite TiO₂ nanoparticles by thermolysis of TiCl₄ on strongly acidic aqueous media. Surf. Sci. 582: 173-188.

[30] Barnard A S, Curtiss L A (2005) Prediction of TiO₂ Nanoparticle Phase and Shape Transitions Controlled by Surface Chemistry. Nano. Lett. 5: 1261-1266.

[31] Gong X Q, Selloni A (2007) First-principles study of the structures and energetics of stoichiometric brookite TiO₂ surfaces. Phys. Rev. B 76: 235307.

[32] Vittadini A, Casarin M, Selloni A (2009) Structure and Stability of TiO₂-B Surfaces: A Density Functional Study. J. Phys. Chem. C Lett. 113: 18973-18977.

[33] Barnard A S, Zapol P (2004) Effects of particle morphology and surface hydrogenation on the phase stability of TiO₂. Phys. Rev. B 70: 235403.

[34] Barnard A S, Zapol P, Curtiss L A (2005) Modeling the Morphology and Phase Stability of TiO₂ Nanocrystals in Water. J. Chem. Theory Comput. 1: 107-116.

[35] Barnard A S, Zapol P, Curtiss L A (2005) Anatase and rutile surfaces with adsorbates representative of acidic and basic conditions. Surf. Sci. 582: 173-188.

[36] Vittadini A, Casarin M, Selloni A (2010) Hydroxylation of TiO₂-B: insights from density functional calculations. J. Mater. Chem. 20: 5871-5877.

[37] Diebold U (2003) The surface science of titanium dioxide. Surf. Sci. Rep. 48: 53-229.

[38] Pang C L, Lindsay R, Thornton G (2008) Chemical Reactions on Rutile TiO₂(110). Chem. Soc. Rev. 37: 2328-2353.

[39] Koizumi S, Watanabe T, Hashimoto K (2001) Effect of repeated photo-illumination on the wettability conversion of titanium dioxide. J. Photochem. Photobio. A 146: 129-132.
[40] Ohno T, Sarukawa K, Matsumura M (2002) Crystal faces of rutile and anatase TiO2 particles and their roles in photocatalytic reactions. New. J. Chem. 26: 1167-1170.

[41] Kawahara T, Konishi Y, Tada H, Tohge N, Nishii J, Ito S (2002) A patterned TiO(Anatase)/TiO(Rutile) Bilayer-Type Photocatalyst: Effect of the Anatase/Rutile Junction on the Photocatalytic Activity Angew. Chem. Int. Ed. 41: 2811-2813.

[42] Gong X Q, Selloni A (2005) Reactivity of Anatase TiO2 Nanoparticles: The Role of the Minority (001) Surface. J. Phys. Chem. B 109: 19560–19562.

[43] Li W K, Gong X Q, Lu G, Selloni A (2008) Different Reactivities of TiO: Polymorphs: Comparative DFT Calculations of Water and Formic Acid Adsorption at Anatase and Brookite TiO2 Surface. J. Phys. Chem. C 112: 6594-6596.

[44] Yang H G, Sun C H, Qiao S Z, Zou J, Liu G, Smith S C, Cheng H M, Lu G Q (2008) Anatase TiO2: single crystals with a large percentage of reactive facets. Nature, 453: 638-641.

[45] Yang H G, Liu G, Qiao S Z, Sun C H, Jin Y G, Smith S C, Zou J, Cheng H M, Lu G Q (2009) Solvothermal Synthesis and Photoreactivity of Anatase TiO2 Nanosheets with Dominant {001} Facets. J. Am. Chem. Soc. 131: 4078-4083.

[46] Zhang D, Li G, Yang X, Yu J C (2009) A micrometer-size TiO2: single-crystal photocatalyst with remarkable 80% level of reactive facets. Chem. Comm. 4381-4383.

[47] Amano F, Prieto-Mahaney O O, Terada Y, Yasmamoto T, Shibayama T, Ohtani B (2009) Decahedral Single-Crystalline Particles of Anatase Titanium(IV) Oxide with High Photocatalytic Activity. Chem. Mater. 21: 2601-2603.

[48] Amano F, Yasmamoto T, Prieto-Mahaney O O, Ueda S, Shibayama T, Ohtani B (2009) Photocatalytic activity of octahedral single-crystalline mesoparticles of anatase titanium(IV) oxide. Chem. Comm. 2311-2313.

[49] Kanie K, Sugimoto T (2003) Organic-Inorganic Hybrid Liquid Crystals: Hybridization of Calamitic Liquid-Crystalline Amines with Monodispersed Anisotropic TiO2 Nanoparticles. J. Am. Chem. Soc. 125: 10518-10519.

[50] Kakihana M, Tada M, Shiro M, Petrykin V, Osada M. Nakamura Y (2001) Structure and Stability of Water Soluble (NH4)4[Ti6(C6H4O7)4(O2)4]·H2O. Inorg. Chem. 40: 891-894.

[51] Kakihana M, Tomita K, Petrykin V, Tada M, Sasaki S, Nakamura Y (2004) Chelating of Titanium by Lactic Acid in the Water-Soluble Diammonium Tris(2-hydroxypropionato)titanate(IV). Inorg. Chem. 43: 4546-4548.

[52] Tomita K, Petrykin V, Kobayashi M, Shiro M, Yoshimura M, Kakihana M (2006) A Water-Soluble Titanium Complex for the Selective Synthesis of Nanocrystalline Brookite, Rutile, and Anatase by a Hydrothermal Method, Angew. Chem. Int. Ed. 45: 2378-2381.

[53] Kobayashi M, Petrykin V, Tomita K, Kakihana M (2008) New water-soluble complexes of titanium with amino acids and their application for synthesis of TiO2 nanoparticles. J. Ceram. Soc. Jpn. 116: 578-583.

[54] Morishima Y, Kobayashi M, Petrykin V, Yin S, Sato T, Kakihana M, Tomita K (2009) Hydrothermal Synthesis of Brookite Type TiO2: Photocatalysts Using a Water-soluble Ti-complex Coordinated by Ethylenediaminotetraacetic Acid. J. Ceram. Soc. Jpn. 117: 320-326.

[55] Kakihana M, Kobayashi M, Tomita K, Petrykin V (2010) Application of Water-Soluble Titanium Complexes as Precursors for Synthesis of Titanium-Containing Oxides via Aqueous Solution Processes. Bull. Chem. Soc. Jpn. 83: 1285-1308.

[56] Truong Q D, Kobayashi M, Kato H, Kakihana M (2011) Hydrothermal synthesis of hierarchical TiO2 microspheres using a novel titanium complex coordinated by picolinic acid, J. Ceram. Soc. Jpn. 119: 513-516.

[57] Yoshizawa M, Kobayashi M, Petrykin V, Kato H, Kakihana M (2013) Insights into a selective synthesis of anatase, rutile and brookite-type titanium dioxides by a hydrothermal treatment of titanium complexes. J. Mater. Res. accepted. DOI:10.1557/jmr.2013.229.

[58] Kobayashi M, Petrykin V, Tomita K, Yoshimura M, Kakihana M (2007) One-step synthesis of TiO2(B) nanoparticles from a water-soluble titanium complex. Chem. Mater. 19: 5373-5376.

[59] Tomita K, Kobayashi M, Petrykin V, Yin S, Sato T, Yoshimura M, Kakihana M (2008) Hydrothermal synthesis of TiO2 nano-particles using novel water-soluble titanium complex. J. Mater. Sci. 43: 2217-2221.

[60] Kobayashi M, Tomita K, Petrykin V, Yoshimura M, Kakihana M (2008) Direct synthesis of brookite-type titanium oxide by hydrothermal method using water-soluble titanium complexes. J. Mater. Sci. 43: 2158-2162.

[61] Munuera G, González-Elipe A R, Fernández A, Maler, Espínos J P (1989) Spectroscopic Characterisation and Photochemical Behaviour of a Titanium Hydroxyperoxo Compound. J. Chem. Soc. Faraday Trans. 1 85: 1279-1290.

[62] Ichinose H, Terasaki M, Katsuki H (1996) Synthesis of Peroxo-Modified Anatase Sol from Peroxo Titanic Acid Solution. J. Ceram. Soc. Jpn. 104: 715-718.

[63] Gao Y, Luo H, Mizusugi S, Nagai M (2008) Surfactant-free Synthesis of Anatase TiO2 Nanorods in an Aqueous Peroxotitanate Solution. Cryst. Growth Des. 8: 3062-3069.

[64] Kobayashi M, Petrykin V, Kakihana M, Tomita K (2007) Morphology control of rutile nanoparticles in a hydrothermal synthesis from water-soluble titanium complex aqueous solution. J Ceram. Soc. Jpn. 115: 835-839.
[65] Kobayashi M, Petrykin V, Kakihana M, Tomita K (2009) Hydrothermal Synthesis and Photocatalytic Activity of Whisker-like Rutile-type Titanium Dioxide. J. Am. Ceram. Soc. 92: S21-S26.

[66] Cheng H, Ma J, Zhao Z, Qi L (1995) Hydrothermal Preparation of Uniform Nanosize Rutile and Anatase Particles, Chem. Mater. 7: 663-671.

[67] Nian J, Teng H (2006) Hydrothermal Synthesis of Single-Crystalline Anatase TiO$_2$ Nanorods with Nanotubes as the Precursor. J. Phys. Chem. B 110: 4193-4198.

[68] Liu Z, Zhang X, Nishimoto S, Jin M, Tyrk D A, Murakami T, Fujishima A (2007) Anatase TiO$_2$ Nanoparticles on Rutile TiO$_2$: Nanorods: A Heterogeneous Nanostructure via Layer-by-Layer Assembly. Langmuir, 23: 10916-10919.

[69] Osada M, Kobayashi M, Kakihana M (2013) Enhanced Dielectric Response Induced by Controlled Morphology in Rutile TiO$_2$: Nanocrystals. J. Ceram. Soc. Jpn. 121: 593-597.

[70] Zhang H, Banfield J F (2000) Understanding Polymorphic Phase Transformation Behavior during Growth of Nanocrystalline Aggregates: Insights from TiO$_2$. J. Phys. Chem. B 104: 3481-3487.

[71] Kobayashi M, Kato H, M Kakihana M (2012) Synthesis of Spindle and Square Bipyramid-shaped Anatase-type Titanium Dioxide Crystals by a Solvothermal Method using Ethylenediamine. J. Ceram. Soc. Jpn. 120: 494-499.

[72] Kobayashi M, Petrykin V, Tomita K, Kakihana M (2011) Hydrothermal synthesis of brookite-type titanium dioxide with snowflake-like nanostructures using a water-soluble citratoperoxotitanate complex. J. Cryst. Growth 337: 30-37.

[73] Ohno Y, Tomita K, Komatsubara Y, Taniguchi T, Katsumata K, Matsushita N, Kogure T, Okada K (2011) Pseudo-Cube Shaped Brookite (TiO$_2$) Nanocrystals Synthesized by an Oleate-Modified Hydrothermal Growth Method. Cryst. Growth Des. 11: 4831-4936.

[74] Niekawa N, Kitamura M (2013) Role of epitaxy-mediated transformation in Ostwald's step rule: a theoretical study. CrystEngComm 15: 6932-6941.

[75] Nada H (2011) Analysis of Ice Crystal Growth Shape under High Pressure Using Molecular Dynamics Simulation. Cryst. Growth Des. 11: 3130-3136.

[76] Sazaki G, Zepeda S, Nakatsubo S, Yokomine M, Furukawa Y (2011) Quasi-liquid layers on ice crystal surfaces are made up of two different phases. Proc. Natl. Acad. Sci. U.S.A. 109: 1052-1055.