Hydrothermal synthesis of hierarchical TiO₂ microspheres using a novel titanium complex coordinated by picolinic acid

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Phase- and morphology-control of TiO₂ was performed by a facile hydrothermal method using a novel water-soluble titanium–picolinato complex as a precursor. Single-phase rutile or brookite type titania can be obtained by tailoring the pH of the complex solution. Rutile with a hierarchical microstructure was synthesized using an excess amount of ligand as an additive and the final product consisted of microspheres with mesopores formed by a self-assembly of nanorods. The anisotropic growth of nanorods with a high aspect ratio was explained by a capping mechanism.

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1. Introduction

Titanium oxide has long been considered to be an important material due to its high performance in various applications such as photocatalysts, sensors, lithium-ion batteries, drug-delivery carriers and dye-sensitized solar cells.¹⁾ The properties of titanium oxide nanoparticles are dependent on the crystalline structure, and anatase, rutile and brookite forms of TiO₂ commonly occur. In addition, the properties of TiO₂ are also influenced by its morphology and microstructures.^{2),3)} Therefore, considerable attention has been given to strategies for the synthesis of TiO₂ with a well-controlled crystalline structure and morphology. In particular, pH control, the introduction of inorganic or organic compounds, or adjustment of precursor concentration have been conducted to obtain TiO₂ with a required structure.^{2)–6)} We have developed a new series of titanium precursors, namely, water-soluble titanium complexes, for the selective synthesis and morphological control of TiO₂ polymorphs.^{7)–10)} For example, size control of brookite and synthesis of rutile nano-whiskers have been achieved using a titanium glycolate complex, in which titanium is coordinated by glycolic acid.^{7)–10)} Many water-soluble titanium complexes with hydroxyl carboxylic acids have been examined to date.^{7)–10)} In view of the coordination chemistry, amino acids are another candidate group of ligands for the formation of stable complexes, because the lone pair of nitrogen and carboxylic acid can be jointly connected to a titanium atom, forming a chelate complex.¹¹⁾ In the search for an amino acid that can be used for the preparation of a titanium complex, picolinic acid (Fig. 1) was found to function as a ligand that produced a stable compound of titanium. It can act as a bidentate ligand for coordination with titanium, because it has an electron-rich nitrogen atom supported by a benzene ring and a carboxy group. Herein, we describe the preparation of a novel water-soluble titanium–picolinato complex and its application as a precursor for the hydrothermal synthesis of brookite nanorods and rutile porous microspheres.

Fig. 1. Structure of picolinic acid.

2. Experiment

TiO₂ was synthesized according to our previously reported method.^{7)–11)} Briefly, a yellow transparent peroxy-titanic acid solution was prepared by adding an ammonia solution (2 cm³, 28%, Kanto Chemicals Co., Inc.) and a hydrogen peroxide solution (10 cm³, 30%, Kanto Chemicals Co., Inc.) to titanium metal (2 mmol, Wako Pure Chemical Industries Ltd.). Picolinic acid (6 mmol, Kanto Chemicals Co., Inc.) was added to the peroxy-titanic acid solution, upon which the solution color changed from yellow to red. Heating at 353 K was necessary to remove excess ammonia and hydrogen peroxide. Finally, a stable red titanium–picolinato complex solution was obtained. The molar amount of picolinic acid should be at least 3 times larger than that of titanium to ensure a stable transparent complex solution. The solution of the complex was diluted to 20 cm³ using distilled water and sealed in a Teflon-lined stainless steel autoclave. The autoclave was heated at 473 K for 24 h, for hydrothermal treatment of the complex, after which the autoclave was allowed to cool to room temperature. The same treatment was carried out for complex solutions with ammonia or picolinic acid as an additive. When the pH of the solution was changed from 6.0 to 10.0 or 4.5 by adding ammonia or picolinic acid, respectively, no precipitation was observed under ambient conditions, although particles were generated after hydrothermal treatment. The resultant powder was separated by centrifugation and washed with distilled water until a neutral pH was obtained. The specimens obtained were then dried at 353 K for 1 day.

The crystalline phase of the samples was characterized using powder X-ray diffraction (XRD; Rigaku RINT V-2200, 40 kV and 30 mA) with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). Data were collected in a 2θ – θ scanning mode with a scan speed of

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Fig. 2. XRD patterns of samples obtained by hydrothermal treatment of a titanium-picolinato complex at (a) pH 4.5 (introduction of 4 mmol picolinic acid as an additive), (b) pH 6.0, and (c) pH 10.0 (adjusted by ammonia addition) (A: anatase, B: brookite, R: rutile).

$4^{\circ} \text{ min}^{-1}$ and a step size of 0.02° . The morphology of the nanoparticles was examined using field-emission scanning electron microscopy (FE-SEM; Hitachi S-4800) at an accelerating voltage of 5 kV. Transmission electron microscopy (TEM; Hitachi H-7650, 100 kV) was conducted using specimens dispersed in ethanol and then dropped onto Cu microgrids coated with a holey carbon film, followed by evaporation of ethanol. N₂ adsorption and desorption isotherms were measured at 77 K (Micromeritics ASAP 2010) to evaluate the adsorption characteristics, Brunauer–Emmett–Teller (BET) specific surface area and Barrett–Joyner–Halenda (BJH) pore size distribution.

3. Results and discussion

Figure 2 shows XRD patterns of TiO₂ particles obtained by hydrothermal treatment of titanium-picolinato complexes at different pH, with or without additives. The particles obtained by hydrothermal treatment of the titanium-picolinato complex at pH 6.0 were composed of rutile and trace amounts of anatase and brookite [Fig. 2(b)]. In contrast, hydrothermal treatment of the alkaline complex solution (pH 10.0) resulted in the production of brookite without impurities [Fig. 2(c)], which was confirmed by precise comparison of the XRD pattern with that simulated using ICSD 036411. The addition of picolinic acid caused the formation of single-phase rutile [Fig. 2(a)].

Figures 3(A) and **3(B)** show TEM images of rutile and brookite particles obtained by hydrothermal treatment of titanium-picolinato complex solutions at pH 6.0 and 10.0, respectively. The rutile prepared at pH 6.0 consisted of spherical, nanorod, or prism shaped particles ranging from 10 to 100 nm. The brookite consisted of nanorods with dimensions of $50 \times 200 \text{ nm}^2$, which were similar to previously reported brookite nanorods synthesized by hydrothermal treatment of a titanium glycolate complex in the presence of NH₃ (aq.) at 473 K for 24 h.^{7,9)} TEM images of the single-phase rutile sample formed at pH 4.5 using picolinic acid as an additive are shown in Figs. 3(C) and 3(D). Spherical particles with diameters of approximately 4 μm and a broken part of a microsphere that

Fig. 3. TEM images of particles synthesized using a titanium-picolinato complex at (A) pH 6.0, (B) pH 10.0 and (C, D) pH 4.5 (with a picolinic acid additive); (C) entire microsphere, and (D) broken part of a microsphere.

Fig. 4. FE-SEM images of TiO₂ microspheres synthesized by hydrothermal treatment of a titanium-picolinato complex with a picolinic acid additive at pH 4.5: (A) low-magnification, (B) high-magnification, (C) top-view, and (D) cross-sectional images.

was several hundred nanometers long are evident. The TEM images illustrate the typically spherical morphology as well as particles radially arranged in dense microspheres.

FE-SEM images of particles synthesized in the presence of picolinic acid (pH 4.5) are shown in **Fig. 4**. The low magnification image shows microspherical particles with diameters of 1 to 4 μm [Fig. 4(A)]. The surface of the microspheres is a porous structure consisting of connected nanoparticles several tens of nanometers in size [Figs. 4(B), 4(C)]. The cross-sectional image of a broken agglomeration shown in Fig. 4(D) indicates that the microspheres are composed of aligned, ordered, and densely packed nanorods that seem to have grown homogeneously from the common center of each sphere.

Fig. 5. Nitrogen adsorption-desorption isotherm of porous TiO_2 microspheres prepared at pH 4.5 and the BJH pore-size distribution curve (inset).

The TiO_2 microspheres synthesized at pH 4.5 were further characterized by N_2 gas adsorption analysis, and the results are shown in Fig. 5. The isotherm curve can be categorized as an IUPAC type III with a hysteresis loop in the range of 0.5–1 P/P_0 . The BET specific surface area was determined to be $44 \text{ m}^2 \text{g}^{-1}$. The pore size distribution was narrow with a maximum of about 22 nm, which was consistent with FE-SEM observations.

In the present work, it was confirmed that the nanorod-based microsphere assembly was critically dependent on the presence of picolinic acid. Hydrothermal treatment of the complex without any additives yielded typical nanoparticles without any specific agglomeration, as shown in Fig. 3(A). Moreover, even if the pH of the starting complex solution was adjusted to around 4.0 using inorganic acids such as hydrochloric, nitric or sulfuric acids, no microsphere morphology was observed. Thus, the presence of picolinic acid, rather than the pH alone, plays an important role in the formation of the oriented organization presented here.

Porous TiO_2 microspheres are applicable for waste water treatment due to their high specific gravity, which allows them to easily settle in the solution after reaction. Numerous methods, including controlled hydrolysis, sol-gel-adding electrolytes, sol-gel spray-coating, and templating spray pyrolysis^{12)–15)} have been proposed for the synthesis of porous TiO_2 microspheres. These methods are based on the sol-gel approach and employ solvents or surfactant templates. The assembly of microspheres has been mediated by various techniques, such as slow polymerization,¹²⁾ control of ionic properties,¹³⁾ spray-coating,¹⁴⁾ or templating.¹⁵⁾ Minimization of the surface energy and liquid surface tension is the general driving force for the self-assembly of microspheres. The removal of organic residue by evaporation or calcination generally produces porous structures. In the present study, it was suggested that microsphere particle growth could be mainly explained in terms of a reduction of the surface energy and the interaction of picolinic acid with the titanium complex precursor and particle interface. A possible scheme for the assembly of nanorods is illustrated in Fig. 6. During the initial stage, narrow nanorods are formed due to the hydrolysis and condensation of the titanium complex precursor in the presence of picolinic acid (1 h reaction time). It also should be mentioned that the nanorods are preferentially organized into a spherical structure to minimize the total surface energy; therefore, the assembly of nanorods into

Fig. 6. (Color online) Schematic illustration of morphological evolution with reaction time with FE-SEM images of particles obtained by hydrothermal treatment of titanium-picolinato in the presence of picolinic acid at 1, 2, and 10 h.

microspheres occurred after 2 h reaction time. The assembly process was probably assisted by a specific interaction of picolinic acid with the titanium complex and the formed particles. Furthermore, the nanorods tended to grow with a particular orientation due to the preferential adsorption of picolinic acid on specific sites of the particle surface, which resulted in the formation of micro-sized nanorods. It is well known that ligands can act as capping reagents, due to chelation with metal at a particle interface.^{2),16)} Therefore, picolinic acid was probably adsorbed to metal rich facets through complex chelation.¹⁰⁾ Further studies on the interaction of picolinic acid with titanium and the formation of unique microsphere are required in order to determine the validity of the proposed mechanism.

4. Conclusions

In summary, rutile- and brookite polymorphs of TiO_2 were selectively synthesized by a facile hydrothermal method using a novel titanium-picolinato complex as a precursor. Brookite particles with typical nanorod shapes were synthesized at pH 10.0. The morphology of rutile could be tuned by the introduction of a ligand additive. In particular, irregular agglomeration of rutile particles was obtained by the treatment of the titanium-picolinato complex without any additives, whereas porous microspheres several micrometers in size, composed of a highly ordered arrangement of nanorods were synthesized in the presence of a picolinic acid additive. It was considered that the growth mechanism of the 3D hierarchical structure was based on the minimization of surface energy and capping chemistry. Our study demonstrated that the desired crystalline structure and morphology can be controlled at the molecular level by selection of a compound with an appropriate coordination architecture.

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