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One-Step Synthesis of TiO_2(B) Nanoparticles from a Water-Soluble Titanium Complex

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We report the first successful synthesis of TiO_2(B) nanoparticles by a one-step hydrothermal process. The process was performed under acidic conditions in a 0.59 M H_2SO_4 solution at 160 °C for 24 h or at 200 °C for 6 h using a titanium metal complex with glycolic acid. The prepared nanoparticles were characterized by XRD, Raman spectroscopy, and TEM. TiO_2(B) is a metastable phase and is one of the most intriguing forms of titanium oxide. All synthesis methods for TiO_2(B) reported to date have required a multistep process involving solid-state synthesis of an alkali metal titanate, an ion-exchange reaction, and gentle dehydration.

Introduction

Titanium dioxide (TiO_2) has long been recognized as an important white pigment. Since the discovery of photoassisted water splitting on a TiO_2 electrode by Honda and Fujishima,[1] this material has also been regarded as an important photocatalyst for possible conversion of optical energy into chemical energy and has been used in solar cells and as an air purifier.[1−6] There are eight polymorphs of titania.[7−14] Among these, only anatase and rutile are employed in practical applications, because they can be easily synthesized. In recent years, it has been reported that, like anatase and rutile, brookite exhibits high photocatalytic activity and hydrophilicity.[15−17] TiO_2(B), a more exotic titania polymorph with a layered structure, has attracted attention as a prospective lithium electrode, sensor material, and photocatalyst.[18−20] Generally, TiO_2(B) is obtained by a three-step procedure. First, $Na_2Ti_3O_7$ or $Na_2Ti_4O_9$ is synthesized by hydrothermal treatment of amorphous $TiO_2{\cdot}nH_2O$, anatase, or rutile in a 10 M NaOH solution.[21,22] Subsequently, the sodium titanate obtained is washed with HCl, which yields $H_2Ti_3O_7$ or $H_2Ti_4O_9$ through an ion-exchange reaction. Finally, the $H_2Ti_3O_7$ or $H_2Ti_4O_9$ is calcined at 400−600 °C to obtain TiO_2(B).[18−20,23,24] The first step of a variant of this method involves the synthesis of $A_2Ti_xO_{2n+1}$ (A = Na, K,

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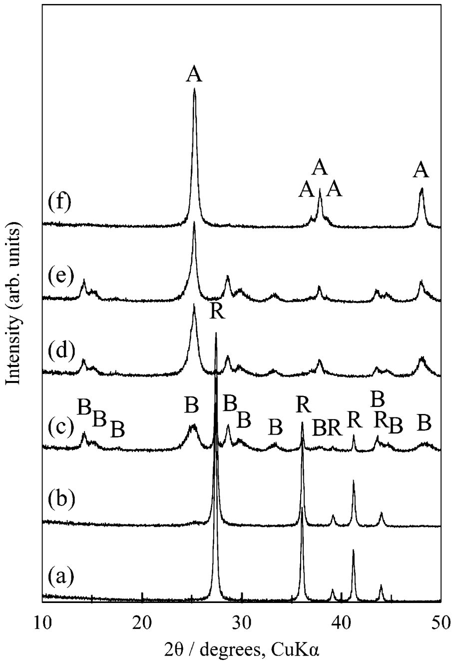

Figure 1. XRD patterns of powders obtained by a 24-h hydrothermal treatment of aqueous titanium glycolate complex solutions at 200 °C containing different amounts of 96% H_2SO_4: (a) 0 mL, (b) 0.27 mL, (c) 0.43 mL, (d) 0.54 mL, (e) 0.65 mL, and (f) 0.82 mL. A, anatase; R, rutile; B, TiO_2(B).

Cs) by the conventional solid-state method using a mixture of TiO_2 and an alkaline metal salt.[9,12]

We have developed a series of water-soluble complexes of titanium.[25−27] Titanium citrate was successfully used in the synthesis of TiO_2 thin-film and $BaTi_4O_9$ photocatalysts by the polymerizable complex method.[27] The titanium glycolate complex was very stable at high pH and could be used for the synthesis of single-phase brookite by a hydrothermal method.[28] This promoted us to investigate whether other unusual polymorphs of titanium dioxide could be obtained by a similarly elegant hydrothermal approach.

In this study, we report the direct synthesis of single-phase TiO_2(B) nanoparticles by hydrothermal treatment of a water-soluble titanium complex solution.

Experimental Section

Synthesis. Metal titanium powder (5 mmol, 98%, Wako Pure Chemical Industries Ltd.) was dissolved in a mixture of H_2O_2 (20 mL, 30.0%, Santoku Chemical Industries Co., Ltd.) and NH_3 (aq) (5 mL, 28%, Kanto Chemicals Co. Inc.). Glycolic acid (7.5 mmol, Kanto Chemicals Co., Inc.) was added into this solution. The resultant solution was heated to 80 °C to eliminate excess H_2O_2 and NH_3. After several hours, the solution turned into a yellow, gel-like substance. This gel was dissolved in water and formed a yellowish transparent solution. Upon the addition of 0, 0.27, 0.43, 0.54, 0.65, or 0.82 mL of H_2SO_4 (96.0%, Kanto Chemicals Co., Inc.) into this aqueous titanium complex solution, the pH changed from 6 to less than 1. Then, the total volume was adjusted to 20 mL by adding water, which yielded a final H_2SO_4 concentration of 0, 0.24, 0.39, 0.49, 0.59, and 0.74 M, respectively. The prepared aqueous solutions were sealed in a Teflon-lined stainless steel autoclave and heated at 120−230 °C for 0.5−100 h. After the autoclave cooled down, the solid products were separated from the solutions by filtration and/or centrifugation. The precipitates were dried at room temperature.

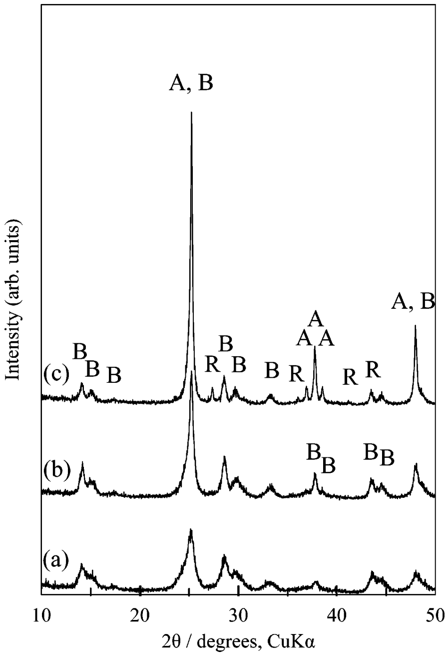

Figure 2. XRD patterns of powders obtained from an aqueous titanium glycolate complex solution containing 0.65 mL of 96% H_2SO_4 (0.59 M) by a 24-h hydrothermal treatment at (a) 160 °C, (b) 200 °C, and (c) 230 °C. A, anatase; R, rutile; B, TiO_2(B).

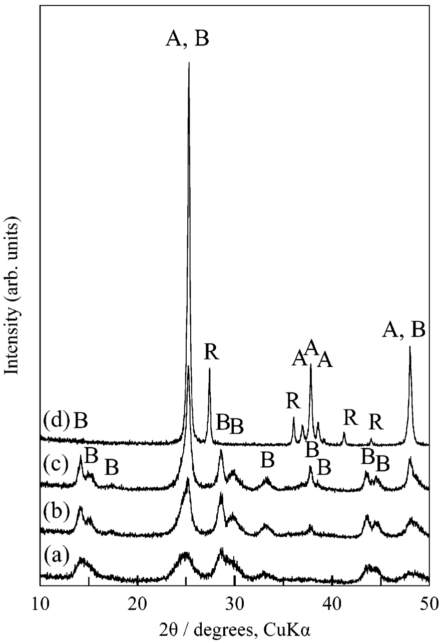

Figure 3. XRD patterns of powders obtained from an aqueous titanium glycolate complex solution with 0.65 mL of 96% H_2SO_4 (0.59 M) by hydrothermal treatment at 200 °C for (a) 1 h, (b) 6 h, (c) 24 h, and (d) 100 h. A, anatase; R, rutile; B, TiO_2(B).

Characterization. X-ray diffraction (XRD) patterns were collected using Cu Kα radiation (wavelength $\lambda = 1.5406$ Å) by a RINT-2200 (Rigaku) operating at 40 kV and 30 mA. The scan speed was 4°/min, and the step size was 0.02°. Raman spectra were

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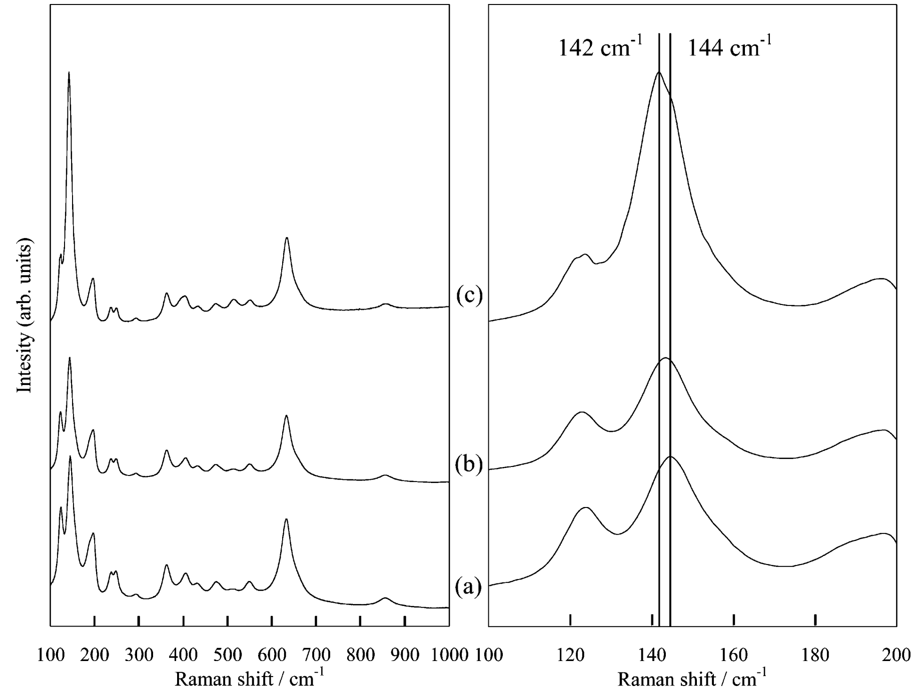

Figure 4. Raman spectra of TiO_2(B) samples synthesized from a titanium glycolate complex with 0.65 mL of 96% H_2SO_4 (0.59 M) by hydrothermal treatment at (a) 160 °C for 24 h, (b) 200 °C for 6 h, and (c) 200 °C for 24 h.

acquired using an NRS-3300 spectrometer (JASCO) in the backscattering geometry. For excitation, a 532.2 nm laser light of 0.1 W power was focused through a microscope into a 2-μm spot on the sample. The scattered light was recorded by a CCD detector, and the monochromator allowed for 1 cm^{-1} resolution. Transmission electron microscopy (TEM) was performed using a LEO912 (Carl Zeiss) operating at 200 kV. The powder sample was suspended in ethanol. One drop of this suspension was transferred onto a Cu microgrid. After evaporation of the ethanol, the sample was used for characterization.

Results and Discussion

According to the XRD and Raman spectroscopy data, all prepared powders consisted of TiO_2 only. Figure 1 shows XRD patterns of samples synthesized by hydrothermal treatment of an aqueous titanium glycolate complex solution with various amounts of H_2SO_4 at 200 °C for 24 h. Without the addition of H_2SO_4 (pH 6), single-phase rutile was obtained (Figure 1a). XRD patterns of the other samples include a characteristic anatase peak at $2\theta = 25.3°$ and a set of reflections from TiO_2(B) at $2\theta = 14.2°$. We note that with increasing H_2SO_4 concentration, rutile gradually diminished, disappearing completely at a H_2SO_4 concentration of 0.59 M (Figure 1e). At the same time, the intensity of TiO_2(B) and anatase reflections increases (Figures 1c−f). However, at very high H_2SO_4 concentration, anatase becomes the only product (Figure 1f). It has been reported that SO_4^{2-} ions inhibit rutile formation and/or promote anatase formation.[29,30] Our results are in good agreement with this hypothesis, since increasing the amount of H_2SO_4 added to the titanium glycolate complex solution led to the formation of less rutile and more anatase. It should be also emphasized that in the absence of H_2SO_4, no TiO_2(B) formed from the aqueous titanium glycolate complex solution at 120−230 °C after 0.5−100 h.

The XRD patterns in Figures 2 and 3 show the effect of the time and temperature of the hydrothermal treatment of the titanium glycolate complex solution at a fixed concentration of the H_2SO_4 on formation of TiO_2 phases. We note that as the synthesis temperature increased from 160 to 230 °C, the intensity of the peak at $2\theta = 25.3°$ due to both TiO_2(B) and anatase increased with respect to the TiO_2(B) peak intensity at $2\theta = 14.2°$ for a constant heat treatment time of 24 h (Figure 2). This indicates that the anatase/TiO_2(B) phase ratio increased with increasing temperature. In addition, the sample obtained at 230 °C contained rutile as the third phase, which has a diffraction peak at $2\theta = 27.4°$. A similar trend was observed for different processing times at a constant temperature of 200 °C (Figure 3). That is, the anatase/TiO_2(B) ratio increased with hydrothermal treatment time, and for very long treatment times, rutile, rather than TiO_2(B), formed as the second phase (Figure 3d). We conducted an additional experiment with the TiO_2(B) sample, whose XRD pattern is presented in Figure 3b. When the TiO_2(B) obtained was heated at various temperatures, the TiO_2(B) phase gradually transformed into anatase with increasing temperature, and single-phase anatase was obtained at 600 °C. Above 700 °C, the rutile phase appeared, while anatase completely transformed into rutile at 900 °C. This experiment demonstrates that TiO_2(B) is presumably the most unstable phase among anatase, rutile, and TiO_2(B).

The best TiO_2(B) powders obtained in this set of experiments were also characterized by Raman spectroscopy. Commercial anatase was used as a reference to identify the anatase peak unambiguously. Figure 4 shows the Raman spectra of the obtained powders. Hydrothermal treatment at 160 °C for 24 h and at 200 °C for 6 h yielded nearly single-

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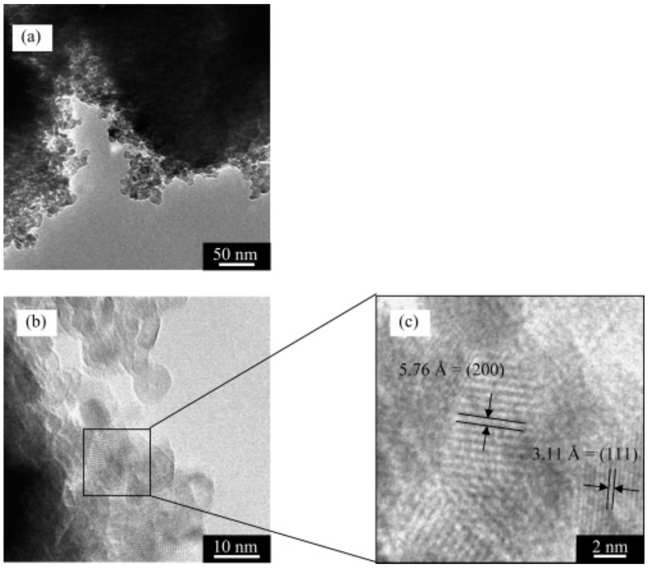

Figure 5. TEM micrographs of powders synthesized by the hydrothermal method at 160 °C for 24 h using a titanium glycolate complex solution with 0.65 mL of 96% H_2SO_4 (0.59 M): (a) low magnification, (b, c) high magnification.

phase TiO_2(B), as revealed by the fact that the Raman spectrum of this sample contained a single peak at 144 cm^{-1} assigned to TiO_2(B)[19,24] (Figure 4a,b). The sample obtained at 200 °C after a longer synthesis time of 24 h contained a peak at 142 cm^{-1} next to the Raman active mode of TiO_2(B) at 144 cm^{-1} (Figure 4c). We assigned this additional peak to anatase on the basis of a comparison with the commercial anatase reference.

Figure 5 shows TEM micrographs of the TiO_2(B) nanoparticles obtained by hydrothermal treatment of the titanium glycolate complex at 160 °C for 24 h with the addition of 0.65 mL of H_2SO_4 (0.59 M solution). The ellipsoidal particles have lattice fringes with a *d*-spacing of 5.76 and 3.11 Å, which correspond, respectively, to the 200 and 111 lattice planes of TiO_2(B) and allow unambiguous identification of the TiO_2(B) phase.

Single-step synthesis of TiO_2(B) by hydrothermal treatment of a titanium metal complex is the most exciting outcome of the present experiments. Although the presence of H_2SO_4 is essential for the formation of TiO_2(B), SO_4^{2-} does not seem to affect the formation of this polymorph directly, because the TiO_2(B) phase cannot be synthesized by a simple hydrolysis of $Ti(SO_4)_2$ or $TiO(SO_4)$. On the other hand, a mixture of TiO_2(B) and anatase could be obtained by hydrothermal treatment of a titanium glycolate complex solution even in the presence of an organic acid, such as citric acid or malic acid, when the pH was adjusted to about 3. Anatase powder containing a small amount of TiO_2(B) could also be obtained from other water-soluble titanium complexes (titanium citrate, titanium lactate, titanium malate, titanium tartrate) in the presence of 0.65 mL of H_2SO_4 (0.59 M), when the heat treatment time was shorter than 6 h and/or the temperature was below 200 °C. Moreover TiO_2(B) appears to be a metastable intermediate phase in the formation of anatase or rutile by the hydrothermal process, and a pH value of around 3 seems to be essential for the onset of TiO_2(B) formation. It has reported that the titania surface tends to adsorb protons at a pH value below 3.5.[31,32] Under the present experimental conditions, where H_2SO_4 or a relatively strong organic acid is used to adjust the pH, the nucleation process is presumably driven toward the formation of protonated species like $H_2Ti_3O_7$ and $H_2Ti_4O_9$, which then lose water and yield a nanocrystalline TiO_2(B) phase. Thus, by controlling the reaction temperature and time, one can easily synthesize TiO_2(B) by a one-step hydrothermal process using a water-soluble titanium complex.

Conclusion

Nanocrystalline single-phase TiO_2(B) was obtained by a one-step hydrothermal treatment of a water-soluble titanium glycolate complex in the presence of 0.59 M H_2SO_4. Phase composition of the samples was determined by XRD and Raman spectroscopy. By controlling the reaction time, temperature, and amount of H_2SO_4 added, anatase and rutile could be synthesized as well. Although H_2SO_4 appears to be important for the synthesis of single-phase TiO_2(B), a mixture of TiO_2(B) with rutile or anatase could also be synthesized by adjusting the pH of the solution to ∼3 using organic acids.

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