

Synthesis of Tubular Titanate via a Self-Assembly and Self-Removal Process

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Novel morphology titanate tubes were successfully synthesized via a self-assembly and self-removal process. After the product was treated by calcinating and washing, crystalline TiO₂ tubes were obtained. In this study, two new concepts are applied to design the synthetic route: (i) titanium glycolate rods obtained from an ethylene glycol-mediated process and titanate sheets synthesized using the hydrothermal process were used as the template and the precursor, respectively, and ii) the template was directly removed in the reaction without posttreatment. Furthermore, a possible mechanism was proposed for the formation of tubular structures.

Introduction

Since the carbon nanotube was discovered in 1991,¹ the synthesis of nanotubes has become one of the most important research subjects in nanotechnology, and various nanotubular materials have been produced during the past decades. TiO₂ nanotubes are particularly interesting, partly because they have large specific surface areas, leading to a wide variety of potential applications in catalysis,² semiconductor devices,³ lithium rechargeable batteries,⁴ and photovoltaic cells.⁵ The exploration of novel approaches for nanostructural TiO₂ of various natures with control of the particle size in the nanometer scale and control of the morphology is quite interesting because the performance of TiO₂ in its various applications depends on its crystalline phase state, dimensions, and morphology.⁶

Until now, several methods, including the replication process,⁷ template technique,⁵ hydrothermal process,^{8–10} and a soft chemical process,¹¹ have been used to prepare TiO₂ nanotubes with different diameters with the nanotubes having single- or multiwall structures. Among them, the TiO₂ nanotube synthesized using the template technique required the removal of the template at a high calcination temperature,⁵ resulting in a collapse of the tubular structure in the product. Thus, a suitable process to directly remove the template in product without a posttreatment procedure is needed. In this study, we first report the synthesis of a tubular titanate with a novel morphology, based on a self-assembly and self-removal process. Further, a possible model was proposed for formation of a novel tubular structure.

Experimental Section

Chemicals. The chemicals used are ethylene glycol (EG, Wako), titanium butoxide solution (Wako), TiO₂ powder (ST-01, Ishihara Sangyo Kaisha, Ltd.), NaOH (Wako), and HCl (35%, Wako).

Preparation of Template and Precursor. Titanium glycolate rods were prepared according to the report.¹² In a typical process, 0.05 mL of titanium butoxide solution was added to a 300 mL flask

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- (1) Ijima, S. *Nature* **1991**, *354*, 56–58.
- (2) Lin, C.; Lee, C.; Chao, J.; Kuo, C.; Cheng, Y.; Huang, W.; Chang, H.; Huang, Y.; Shih, M. *Catal. Lett.* **2004**, *98*, 61–66.
- (3) Vinodgopal, K.; Hotchandani S.; Kamat, P. *J. Phys. Chem.* **1993**, *97*, 9040–9044.
- (4) Li, J. R.; Tang Z. L.; Zhang, Z. T. *Electrochem. Commun.* **2005**, *7*, 62–67.
- (5) Adachi, M.; Murata Y.; Harada, M. *Chem. Lett.* **2000**, *29*, 942–943.
- (6) Melendres, C.; Narayanasamy, A.; Maroni A.; Siegel, W. *J. Mater. Res.* **1989**, *4*, 1246–1250.

- (7) Hoyer, P. *Langmuir* **1996**, *12*, 1411–1413.
- (8) Kasuga, T.; Masayoshi, M.; Hoson, A.; Sekino T.; Niihara, K. *Langmuir* **1998**, *14*, 3160–3163.
- (9) Seo, D. S.; Lee J. K.; Kim, H. J. *Cryst. Growth* **2001**, *229*, 428–432.
- (10) Wang, Y. Q.; Hu, G. Q.; Duan, X. F.; Sun H. J.; Xue, Q. K. *Chem. Phys. Lett.* **2002**, *365*, 427–341.
- (11) Wei, M. D.; Konishi, Y.; Zhou, H. S.; Sugiara H.; Arakawa, H. *Solid State Commun.* **2005**, *133*, 493–497.

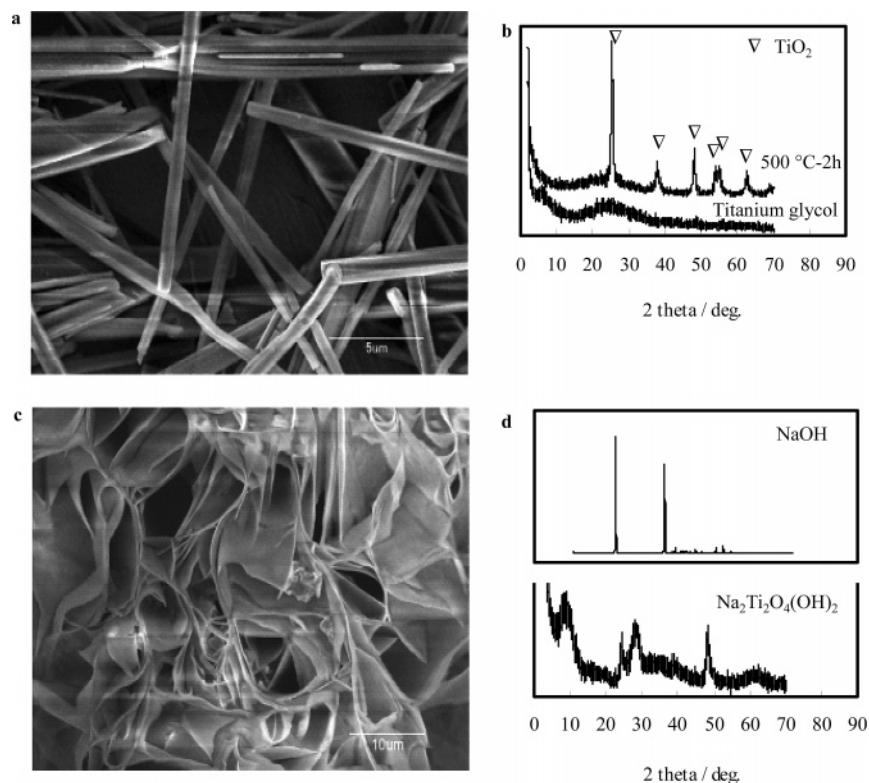


Figure 1. SEM images and XRD patterns of the synthesized template and precursor. (a) SEM image of titanium glycolate rods synthesized at 170 °C for 2 h. (b) XRD patterns of titanium glycolate rods before and after calcination at 500 °C for 2 h. (c) SEM image of titanate sheets synthesized using 10 M NaOH at 100 °C for 7 days (unwashed). (d) XRD patterns of titanate sheets washed (below) and unwashed (upper) with deionized water.

that contained 10 mL of ethylene glycol (EG), and then the mixture was heated at 170 °C in an oil bath with magnetic stirring for 2 h. After the white product formed, the solution was cooled to room temperature, and the product was washed with deionized water. Finally, the white product was dried at 50 °C for 4 h, and the titanium glycolate rod was obtained. The as-synthesized product (titanium glycolate rods) was not calcined and was used directly as a template in the self-assembly process.

Titanate sheets were synthesized according to the report with a minor modification.⁸ In a typical process, 0.5 g of TiO₂ and 100 mL of an NaOH solution (10 M) were placed in a 250 mL Teflon flask in an oil bath at 100 °C for 2–10 days. The product was not washed and was used directly as a precursor in the synthesis process.

Synthesis of Sample. In this synthetic route, a titanium glycolate rod (crude product) was used as a template, and a titanate sheet (unwashed) was used as a precursor. In a typical procedure, 0.15 g of template and 1.0 g of precursor were mixed in 80 mL of H₂O under magnetic stirring, and then the mixture was placed in a 100 mL Teflon-lined autoclave at 170 °C for 2–7 days. Finally, the as-synthesized product was dried in an oven at 70 °C for 4 h and was used for further characterization.

Characterization of Samples. X-ray powder diffraction (XRD) patterns were recorded using a diffractometer (Mac Science). Scanning electron and transmission electron micrographs (SEM and TEM, respectively) were taken on a TOPCON DS instrument and a JEOL instrument, respectively. Laser Raman and FT-IR spectra of the samples were determined with JASCO VENTURE21 and JASCO FT/IR-6200 instruments, respectively.

Results and Discussion

Figure 1 shows SEM images and XRD patterns of the titanium glycolate rods and titanate sheets. Figure 1a reveals

the presence of numerous rods with typical lengths ranging from several micrometers to several tens of micrometers, and their diameters are ca. 0.5–2 μm. This is also in agreement with the report by Jiang et al.¹² XRD patterns of titanium glycolate rods before and after calcination are depicted in Figure 1b. It was found that anatase TiO₂ was formed after the crude product was calcined at 500 °C for 2 h, during which organic compounds were removed. The SEM image of the titanate sheets is depicted in Figure 1c. A large number of sheets are aggregated together. The size of the sheets is more than 10 × 10 μm, and the thickness is ca. 10–20 nm. The XRD patterns of the product without washing are depicted in Figure 1d (upper). Only the NaOH phase was observed for the unwashed product because the high concentration of NaOH in the product was not removed. After it was washed with the deionized water, until a pH value near 7, a layered titanate was obtained. As shown in Figure 1d (below), all reflections could be indexed onto Na₂Ti₂O₄(OH)₂ according to a more recent report.^{13,14}

A series of products were synthesized at different reaction times and observed by SEM and TEM. Figure 2 shows SEM images of products obtained at 7 days and their derivatives after heat treatment and washing with dilute HCl (0.1 M). Numerous tubular structures are found in the product, as depicted in Figure 2a. The length of tubes is ca. several

(12) Jiang, X.; Wang, Y.; Herricks T.; Xia, Y. *J. Mater. Chem.* **2004**, *14*, 695–703.

(13) Zhang, M.; Jin, Z. S.; Zhang, J. W.; Guo, X. Y.; Yang, J. J.; Li, W.; Wang X. D.; Zhang, Z. J. *J. Mol. Catal. A* **2004**, *217*, 203–210.

(14) Yang, J. J.; Jin, Z. S.; Wang, X. D.; Li, W.; Zhang, J. W.; Zhang, S. L.; Guo X. Y.; Zhang, Z. J. *Dalton Trans.* **2004**, 3898–3901.

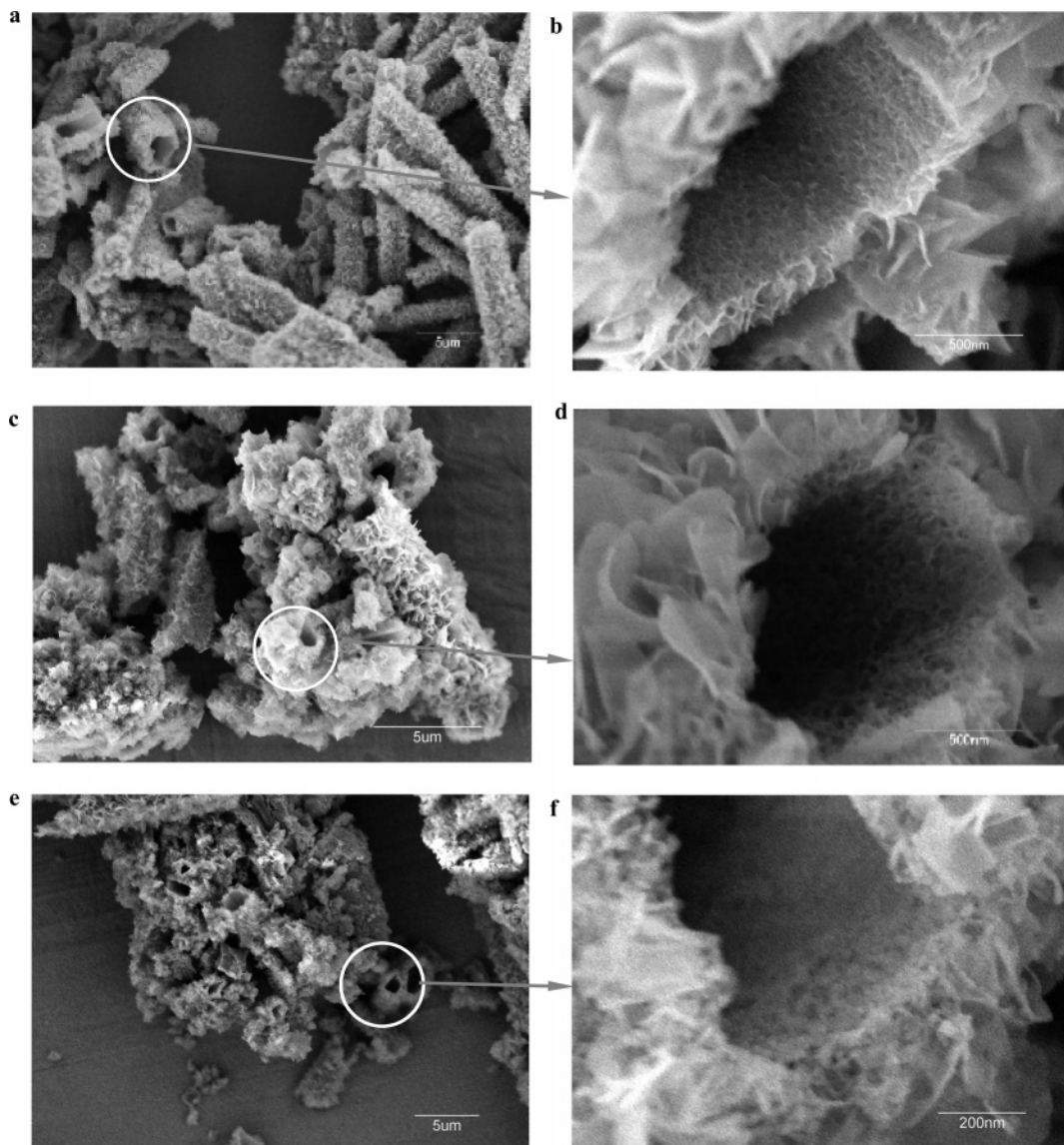


Figure 2. SEM images of the products synthesized at 170 °C for 7 days and their derivatives after treatment by calcination and washing: (a and b) the starting product, (c and d) the starting product after calcination at 500 °C for 2 h, and (e and f) the calcined product that was stirred in dilute HCl for 24 h and then further calcined at 500 °C for 2 h.

micrometers to several tens of micrometers. A high magnification image of the open end of a single tube reveals that the wall is composed of aggregated sheets. The inner diameter is ca. 0.5–1 μm , and the wall thickness is ~ 200 nm. The starting products were calcined at 500 °C for 2 h, and their SEM images are depicted in Figure 2c–d. It is found that the tubular structures can be retained, indicating that tubular structures have a thermal stability. To remove the residual Na^+ ions in the product, the calcined samples were stirred in 0.1 M HCl solution for 24 h, and then were further calcined at 500 °C for 2 h. As shown in Figure 2e–f, the tubular structure of treated sample is also not collapsed.

To confirm the hollow nature of tubes, the same samples mentioned above were measured by TEM, as shown in Figure 3. Figure 3a shows the hollow nature of the tubes with an open end. The inner diameter and wall thickness are the same as those observed in SEM images. It can be seen from Figure 3b that a larger number of sheets aggregated

to form the walls. The EDX spectrum, as depicted in Figure 3c, indicates that the product contains Na^+ ions. The starting product was calcined 500 °C for 2 h and observed by TEM, as depicted in Figure 3d. The tubular structure of calcined products is almost unchanged, and this is also apparent in the TEM image of a cross-section of a tube (see Figure 3f). A high magnification TEM image of the sheets on the surface of a tube is depicted in Figure 3e. It clearly shows that the wall is composed of sheets with ca. 10 nm of thickness. Figure 3g shows a TEM image of the sample calcined at 500 °C for 2 h that was stirred in a 0.1 M HCl solution for 24 h and then further calcined at 500 °C for 2 h. It clearly indicates that the tubular structure of products can be maintained very well. A high magnification image of a sheet on the surface of tube is depicted in Figure 3h, indicating that the walls of the tubular structures are composed of crystallized sheets, and the lattice fringes correspond to a d spacing of 0.32 nm. As shown in Figure 3i, the EDX

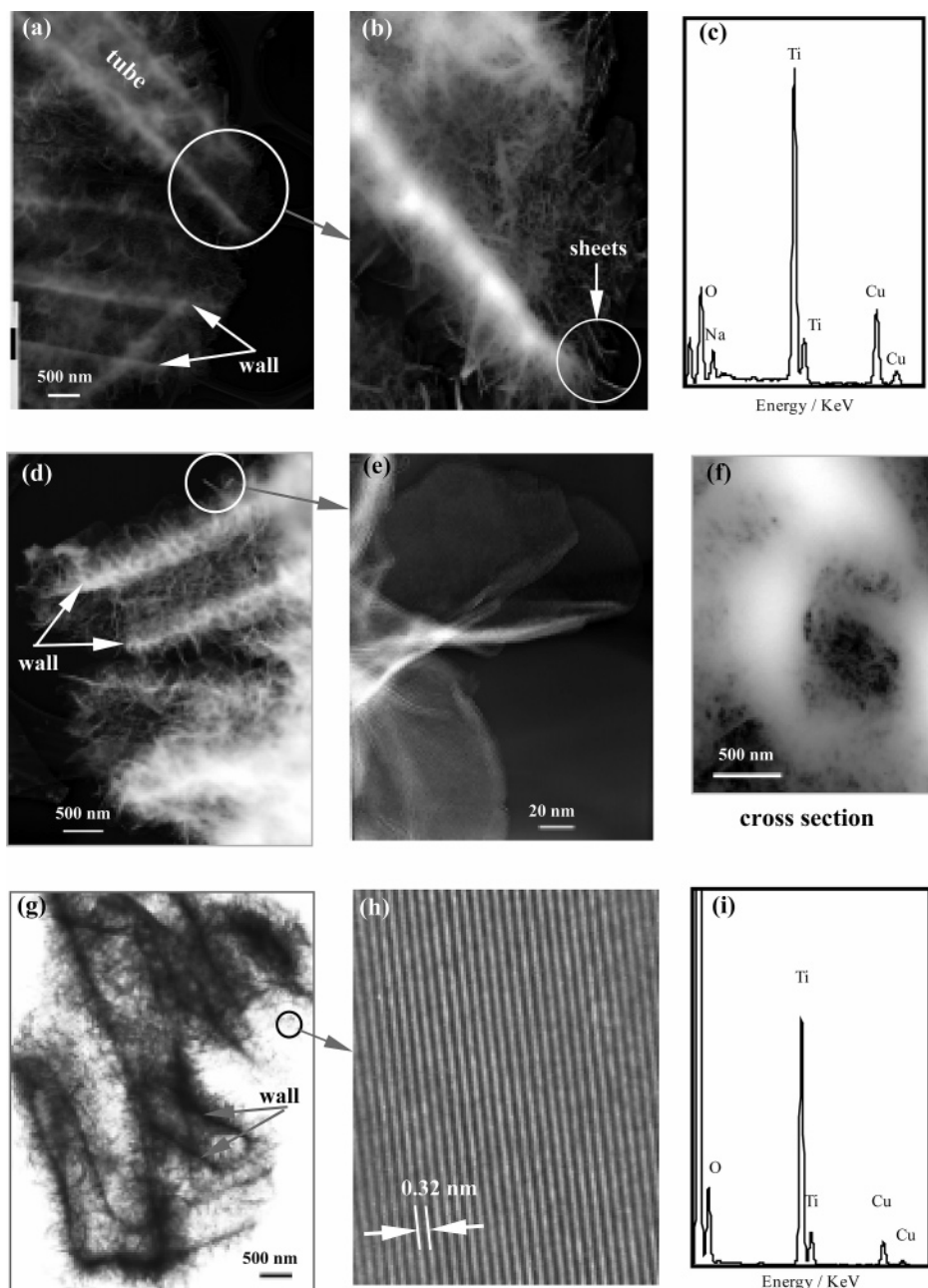


Figure 3. TEM images of the products synthesized at 170 °C for 7 days and their derivatives after treatment by calcination and washing: (a) the starting product, (b) high-magnification image of a single tube, (c) EDX spectrum, (d) the starting product after calcination at 500 °C for 2 h, (e) high-magnification image of sheets on the surface of a tube, (f) the cross section of a single tube, (g) the calcined product that was stirred in dilute HCl for 24 h and then further calcined at 500 °C for 2 h, (h) the high-magnification image, and (i) the EDX spectrum.

spectrum confirms that the residual Na^+ was not detected after the starting products were treated by being washed in the dilute HCl solution.

Figure 4 shows XRD patterns of the same samples measured by SEM and TEM. As depicted in Figure 4a, the XRD patterns of starting products could be indexed to $\text{Na}_2\text{-Ti}_3\text{O}_4(\text{OH})_2$, according to current structural investigations.^{13,14} After the starting products were calcined at 500 °C for 2 h, the crystal phase was not changed, as shown in Figure 4b. Sun et al.¹⁵ investigated the effect of residual Na^+ on the thermal stability of titanate nanotubes synthesized using the

hydrothermal process² and found that the thermal stability of the titanate nanotubes was strongly dependent on the presence of Na^+ ions. In this study, we also investigated the effect of residual Na^+ ions on the thermal stability of the products. The calcined sample mentioned above was stirred in a 0.1 M HCl solution for 24 h to remove the Na^+ ions in products and was then further calcined at 500 °C for 2 h. As depicted in Figure 4c, the reflections are significantly different from those of the untreated sample. The reflection at ca. 10° completely disappeared, indicating a structure change. All the reflections can be indexed into anatase TiO_2 (JCPDS 21-1272) and rutile TiO_2 (JCPDS 01-1292), indicat-

(15) Sun, X. M.; Li, Y. D. *Chem.—Eur. J.* **2003**, *9*, 2229–2238.

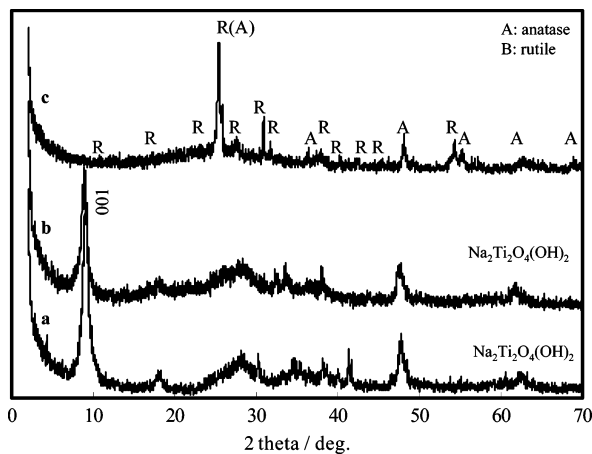


Figure 4. XRD patterns of the products synthesized at 170 °C for 7 days and their derivatives after treatment by calcination and washing: (a) the starting product, (b) the starting product after calcination at 500 °C for 2 h, and (c) the calcined product that was stirred in dilute HCl for 24 h and then further calcined at 500 °C for 2 h.

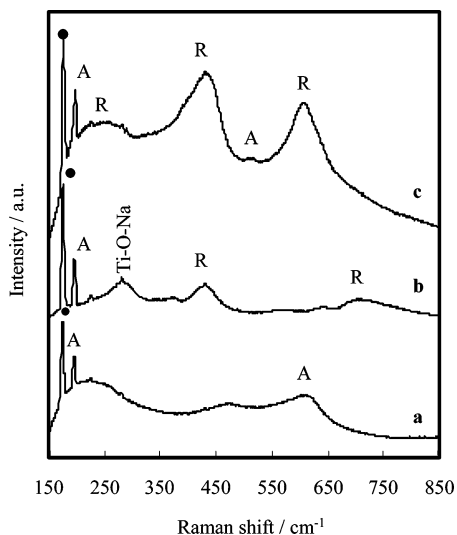


Figure 5. Laser Raman spectra: (a) template (titanium glycolate rods), (b) the starting product synthesized at 170 °C for 7 days, and (c) the final product (the starting product after calcination at 500 °C for 2 h, followed by stirring in dilute HCl for 24 h and further calcining at 500 °C for 2 h) (A, anatase phase; R, rutile phase; ●, substrate).

ing that the final products are composed of anatase and rutile TiO_2 . Therefore, the starting product titanate tubes can be transferred into crystal TiO_2 tubes without collapse of tubular structure using a sintering and washing treatment.

Figure 5 shows the laser Raman spectra of the template (titanate glycolate rods) and the starting product synthesized at 170 °C for 7 days, as well as their derivatives after the posttreatments. The Raman peaks at 197 and 630 cm^{-1} in Figure 5a are from the Ti–O bonds of the anatase, in agreement with the report.¹⁶ After the template was calcined at 500 °C for 2 h, six Raman peaks are observed (see Supporting Information). As depicted in Figure 5b, the Raman spectrum of the starting product is different from the template. The peaks at 197 and 442 cm^{-1} are assigned to the anatase and rutile phases, respectively.^{16,17} According to

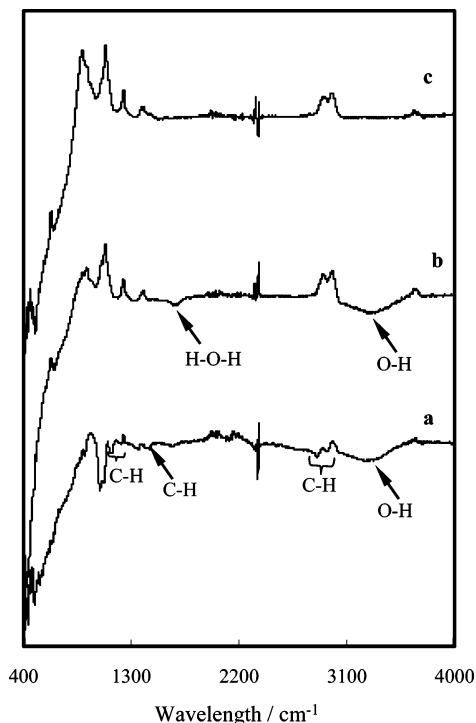


Figure 6. FT-IR spectra: (a) template (titanium glycolate rods), (b) the starting product synthesized at 170 °C for 7 days, and (c) the final product (the starting product was calcined at 500 °C for 2 h, then it was stirred in dilute HCl for 24 h, and then calcined again at 500 °C for 2 h).

the report,¹⁶ the peaks at 707 cm^{-1} may come from defects in the crystal. The peak at 284 cm^{-1} was suggested to be from Ti–O–Na, as reported for Na_2O – TiO_2 glass.¹⁸ After the starting products were calcined at 500 °C for 2 h, they were stirred in a 0.1 M HCl solution for 24 h to remove the residual Na^+ in the products. When the treated products were calcined at 500 °C for a further 2 h, the final products were obtained. As depicted in Figure 5c, the peaks at 197 and 513 cm^{-1} are assigned to the E_g and A_{1g} modes for the anatase phase,¹⁶ and the peaks at 442 and 612 cm^{-1} are the E_g and A_{1g} modes for the rutile phase.¹⁷ The wide band at 220–280 cm^{-1} for a typical rutile phase results from a second reflection or defects.¹⁹

Figure 6 shows the FT-IR spectra of the same samples that were measured by laser Raman spectroscopy. The band at 3400 cm^{-1} in Figure 6a is assigned to the stretching of the O–H bond, and the bands at 2840–3000 cm^{-1} are assigned to the stretching of C–H bonds of the $-\text{CH}_2$ groups.^{20,21} At approximately 1465 cm^{-1} a signal corresponding to the bending of $-\text{CH}_2$ groups appears, and the bands at 1150–1350 cm^{-1} are assigned to the scissoring of the C–H bonds of the $-\text{CH}_2$ groups.^{20,21} In Figure 6b, the stretching of the O–H bond in the starting products is also

(16) Choi, H. C.; Jung, Y. M.; Kim, S. B. *Vib. Spectrosc.* **2005**, *37*, 33–38.

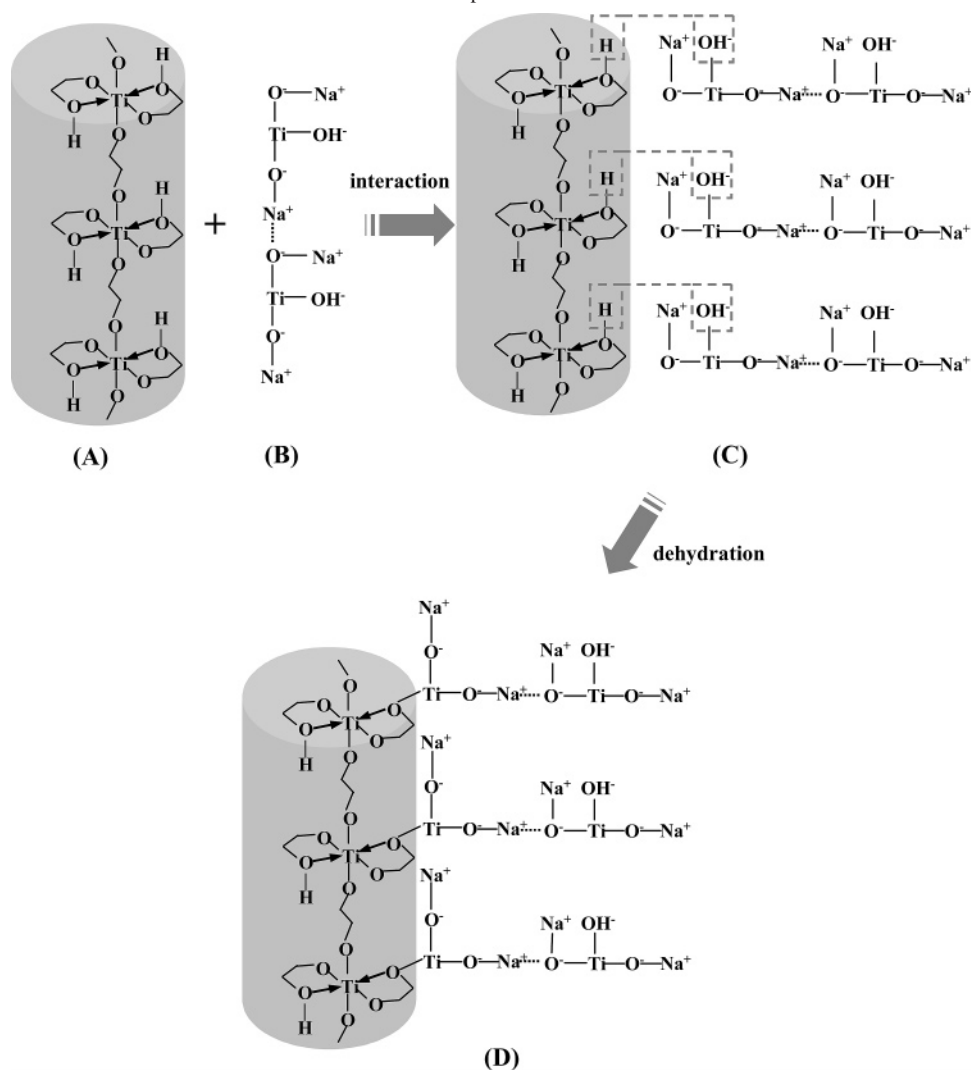
(17) Li, X. J.; Kobayashi, T.; Sekine, T. *Solid State Commun.* **2004**, *130*, 79–82.

(18) Kim, H. M.; Miyaji, F.; Kokubo, T.; Nakamura, T. *J. Mater. Sci. Mater. Med.* **1997**, *8*, 341–347.

(19) Balachandra, U.; Eror, N. G. *J. Solid State Chem.* **1982**, *42*, 276–282.

(20) Domínguez, A. M.; Záratea, A.; Quijada, R.; López, T. *J. Mol. Catal. A* **2004**, *207*, 153–159.

(21) Silverstein, R. M.; Webster, F. X. *Spectrometric Identification of Organic Compounds*; John Wiley & Sons: New York, 1998.

Scheme 1. Possible Formation Mechanism of the Tubular Titanate Composed of Sheets^a

^a (A) template (rodlike, linear complexes between ethylene glycol and titanium, ref 12); (B) precursor (sheets, layered $\text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2$, ref 13–14); (C) interaction between the template and precursor; and (D) mixture composed of template and precursor after dehydration.

observed. After the starting products were treated by calcination and washing, the bands of O–H and C–H are not observed, as depicted in Figure 6c. This indicates that the organic components were removed from the final products by the posttreatments.

In the traditionally synthetic routes, the surfactant was directly applied to synthesize nanomaterials with a tubular structure, and then it was removed by washing or calcination at high temperature. However, in this study, new concepts were applied to synthesize novel morphology tubes composed of sheets. Our synthetic route is based on self-assembly between the precursor and template, as well as on the self-removal of the template during the reaction. On the basis of the results mentioned above, a possible formation mechanism for a tubular structure composed of sheets was illustrated in Scheme 1. Titanium glycol rods prepared using an ethylene glycol-mediated process were used as template. According to the report on the growth mechanism,¹² the linear complexes were formed between ethylene glycol (EG) and titanium and could further aggregate into 1D nanostructure (Scheme 1A). As the precursor, titanate sheets, $\text{Na}_2\text{Ti}_2\text{O}_4-$

$(\text{OH})_2$, have a layered structure (Scheme 1B).^{13,14} When the template and the precursor were mixed in an autoclave at 170 °C for several days, an interaction occurred between the –O–H in the ethylene glycolate titanium and the –O–H in $\text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2$ (Scheme 1C). The former was coordinated with Ti^{4+} to form TiO_6 octahedra, and the weakened O–H bond resulted in the O–H bond tend to be broken and react with the latter to produce H_2O . Finally, a mixture composed of the template and precursor was formed via –O–Ti– bond connections (Scheme 1D). Obviously, this is a self-assembly process. When a large number of sheets were aggregated on the surface of template (rodlike), cylinder-like mixtures were formed. Namely, the rods, as a core, were surrounded by sheets, and the sheets with cured edges were aggregated together. After the template was dissolved from the cylinder-like mixtures, the hollow structure was formed. Therefore, the inner diameters of the tube in the products are almost same as the diameters of the template (rods). The dissolution of the template might be attributed to the reaction between the template and an NaOH solution with higher concentration. As mentioned above, the precursor without washing

Table 1. Reaction Results Using the Treated Template or Precursor under Same Conditions

precursor	template	product	comment
titanium glycolate rods (TGN)	titanate sheets	tubes	Figures 2 and 3
calcined TGN (500 °C for 2 h)	titanate sheets	rods	Supporting Information 2
ethylene glycol (EG)	titanate sheets	sheets	Supporting Information 3

was directly applied in this reaction. Thus, the NaOH concentration in reaction solution is high (pH > 14). Under a high concentration of NaOH, the Ti^{4+} in the template (rods) reacted with the NaOH to form titanate sheets. As a result, the template was dissolved in the reaction. On the other hand, titanate sheets were provided, as a precursor, to form the wall of tubes in synthetic reaction. This is the reason that the template was not detected in the products. Therefore, the dissolution of the template is a self-removal process.

To confirm the formation model suggested above, the synthesis process using treated template and EG was executed under the same reaction conditions. (i) The template (titanium glycolate rods) was calcined at 500 °C for 2 h to obtain anatase TiO_2 rods (see Figure 1b and Supporting Information 1), and then the anatase TiO_2 rods replaced titanium glycolate rods as the template. (ii) EG replaced the titanium glycolate rods and used it as a template. The reaction results are listed in Table 1. It was found that no tubular structure was formed in the products for the above reactions (see Supporting Information 2 and 3), indicating that titanium glycolate rods play an indispensable role in the formation of the tubular structure in this synthesis route. From the above results, the self-assembly model via interaction between titanium glycolate rods and titanate sheets and the self-removal model via dissolution of the template in the reaction

could be used to explain the formation of the tubular structure.

Conclusions

We have successfully synthesized novel morphology tubular titanates via a self-assembly and self-removal process. The walls of these tubes are composed of sheets, and their inner diameter is ca. several hundred nanometers. After the starting products were treated by calcination and washing, crystalline TiO_2 tubes can be obtained. In this study, the synthesis of novel morphology titanate is based on new concepts. First, the as-synthesized products, titanium glycolate rods obtained from ethylene glycol-mediated process and titanate sheets synthesized using the hydrothermal process, were used as the template and the precursor, respectively. In general, organic compounds or surfactants are often used as template, and the solution or colloid-containing metals ions were used as the precursor. Second, the template was directly removed in the reaction without posttreatment via a self-removal process. This is very different from the traditionally synthetic routes, in which the organic compound or surfactant was directly used as a structure-directing template and then removed from the product by washing with H_2O /EtOH or calcination at high temperature. We believe that such a self-assembly and self-removal process, based on new concepts, has the potential to prepare nanostructural metal oxides with novel morphologies.

Supporting Information Available: Figures showing a laser Raman spectra of the calcined template and SEM images, N_2 adsorption–desorption isotherms, and pore size distributions of the products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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