Langmuir **2007,** *23,* 10333−10341

Fabrication of Size-Tunable TiO_2 Tubes Using Rod-Shaped Calcite Templates

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Received May 8, 2007. In Final Form: July 17, 2007

Titania tubes with tunable wall thickness were produced by the sol−gel reaction of titanium(IV) *n*-butoxide in the presence of rod-shaped calcite particles that act as templates. A shell of amorphous titania was deposited around the calcite particles by sol−gel synthesis. The titania was crystallized to the anatase or rutile phase by sintering at different temperatures, and then acid etching was used to remove the calcite core, leaving hollow titania tubes. The influences of several parameters on the final particle formation were investigated, including calcite templates, surfactant, the method of adding reagents, and catalyst. The average width of the prepared titania tubes ranges from nearly 100 nm to 1 μm, with wall thickness ranging from approximately 70 to 300 nm. A possible growth mechanism of the titania tubes is presented. The ability to control titania tube size and crystal structure is important for photocatalysis, photovoltaics, and other applications. The fabrication approach presented is applicable to form tubes of other oxide materials by sol−gel synthesis.

Introduction

Titania (TiO_2), a metal oxide semiconductor, has been extensively investigated in a variety of fields due to its unique electrical, optical, chemical, and physical properties. Because of its excellent thermal stability, high electron mobility, and wide band gap between the valence and conduction bands,[1,2] TiO_2 is used as an electrode in dye-sensitized photovoltaic cells[3−5] and as a water-splitting catalyst for hydrogen generation.[6−8] TiO_2 has been considered an ideal candidate for fabricating photonic crystals due to its low absorption in the visible and near-infrared regions and its high refractive index.[9,10] The electrical conductance of TiO_2 increases markedly upon exposure to H_2, making it a promising material for H_2 sensing.[11−13] Mesoporous TiO_2 is an important support material for other catalysts.[14,15] TiO_2 has also been used as a hygroscopic additive in polymer fuel cell membranes to maintain water content, and thus proton conductivity, under high-temperature operating conditions[16−18] In all applications mentioned above, the performance of TiO_2 depends on its structure, size, and crystallinity, as these variables influence catalytic activity, optical properties, surface properties, and surface area available for adsorption.[19−22] Therefore, controlled crystallization and crystal assembly of titania are important issues for current research.

One-dimensional nanostructured materials such as tubes have attracted widespread interest for a wide range of applications.[23] TiO_2 tubes, with large specific surface area and high surface-to-volume ratio, have shown improved performance over particles used in photocatalysis,[14,24,25] sensing,[11,12] luminescence,[26] and photovoltaics.[27] As a result, considerable effort has been focused on developing efficient methods of fabricating titania tubes of controllable size and surface properties. Anodic oxidation of titanium foil has been demonstrated as an effective approach to prepare titania tubes.[28] Titania arrays with average tube diameters from 25 to 65 nm were obtained by employing this method. However, anodic oxidation does not produce individual tubes but rather a “honeycomb-like” film with interconnecting tube walls. In addition, the tubular structure within the film is disrupted at high temperature due to oxidation and grain growth in the

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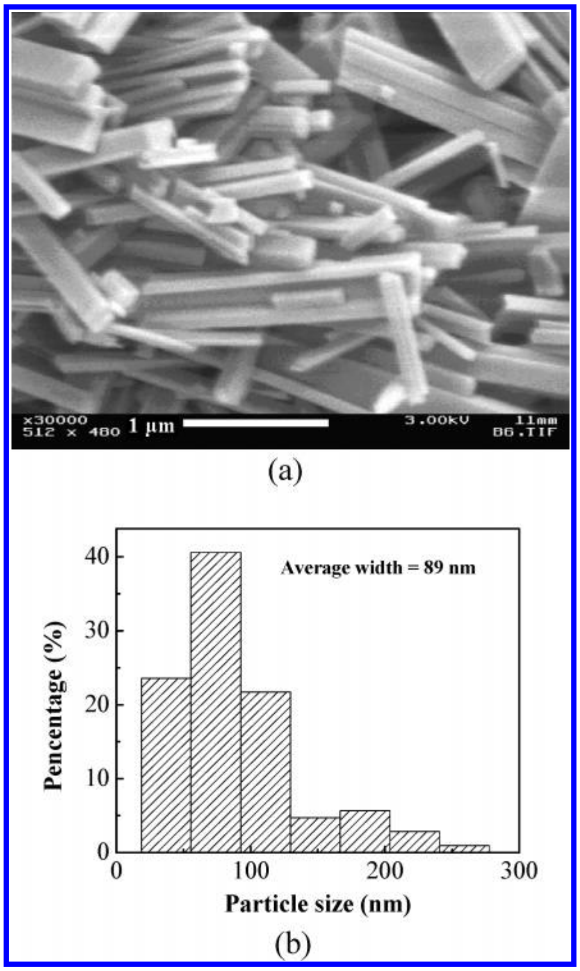

Figure 1. Calcite templates employed for synthesis of titania tubes: (a) SEM image showing particle morphology and (b) histogram of particle width distribution.

titanium support.[29] Alkaline hydrothermal synthesis provides a route to prepare individual TiO_2 nanotubes with diameters of about 8−10 nm and lengths of around 50−200 nm.[30,31] Because of the small particle size, titania nanotubes obtained by alkaline hydrothermal synthesis tend to aggregate, and high-temperature calcination results in the destruction of the tubular structure.[20] Electrospinning is another approach used to produce titania nanotubes with independently varied particle size and wall thickness through controlling the experimental parameters.[32] However, no data has been reported on stable TiO_2 tubes calcinated under high temperature, at which the TiO_2 transforms to the rutile crystalline phase.

Nanotubes can also be formed by sol−gel synthesis of TiO_2 on the surface of sacrificial templates. Although templated synthesis is more tedious in comparison with the above two schemes, it offers a more flexible way to vary tube dimensions and surface structure. In a typical procedure, template particles are suspended in a TiO_2 precursor solution that forms a sol by hydrolysis and aggregates into a gel network by subsequent condensation. The template particles are coated with amorphous TiO_2 by controlled surface precipitation during sol−gel synthesis to create core−shell composites. Finally, the template is removed by selective dissolution in an appropriate solvent or by calcination at an elevated temperature to generate titania tubes with the shape mimicking that of the employed template. TiO_2 tubes have been prepared by templating against porous anodic alumina membranes,[33] ZnO nanorods,[34] supramolecular assemblies,[35] and electrospun polymers.[36]

We recently reported the synthesis and characterization of a new rod-shaped morphology of calcite.[37] In the present work, we use these novel rod-shaped calcite crystals as templates for the sol−gel synthesis of titania tubes. In this approach, uniform and size-tunable titania tubes can be easily obtained. The as-prepared tubes keep their tubular structure after high-temperature annealing and acid etching to remove calcite. The TiO_2 tubes prepared by this new synthetic approach can be aligned and assembled in a hierarchical manner and are expected to find application in solar cells, fuel cells, and other devices. The synthetic approach may also be used to form tubes of other materials synthesized by sol−gel chemistry.

Experimental Section

Materials. Cetyltrimethylammonium bromide (CTAB) was purchased from J.T. Baker. Titanium(IV) *n*-butoxide (97% purity) and *n*-butanol (99.4%, ACS reagent grade) were purchased from Aldrich. Hydrochloric acid (HCl) was supplied by Mallinckrodt Chemicals (ACS reagent grade) with a concentration of 37.1%. The calcite templates were prepared following a synthetic procedure previously reported.[37] Absolute ethanol (Pharmco products, Inc.) and deionized water were used.

Preparation of TiO_2-Coated Calcite Composites. The sol−gel reaction was started by dispersing 20-mg of calcite template particles in 16 mL of *n*-butanol using an ultrasonic bath (Aquasonic model 75T, VWR Scientific Products). After ∼5 min, a homogeneous opaque suspension was formed. Twenty milligrams of CTAB and 0.5 mL deionized water were then added in sequence. The suspension was mixed for 45 min by mild stirring before adding any other reactants. A desired amount of titanium(IV) *n*-butoxide was diluted with 10 mL *n*-butanol in a 20-mL glass vial to form the TiO_2 precursor. A syringe pump (Pump 11, Harvard Apparatus) was used to feed the TiO_2 precursor solution into the calcite suspension at a rate of 0.865 mL/h. After addition of the TiO_2 precursor solution, the suspension became milky white. Stirring was continued for 12 h to complete the condensation reaction of TiO_2. Everything was carried out at room temperature. The product was collected by centrifugation at 8000 rpm for 5 min and then washed by dispersing in absolute ethanol. The ethanol washing and centrifugation steps were repeated three times. A vacuum oven was utilized to dry the wet product at room temperature overnight.

Formation of TiO_2 Tubes. The as-synthesized titania−calcite composites were calcined in a tube furnace (TF55030, Lindberg/Blue Mini-Mite Tube Furnace) in air. The samples were heated to the desired temperature at a rate of 10 °C/min and then were maintained at that temperature for 2 h. Afterward, the particles were allowed to cool to room temperature. Then, the particles were placed in 1 M HCl for 12 h to remove the calcite core. The TiO_2 tubes were collected by centrifugation at 8000 rpm for 5 min and washed three times by dispersing the particles in deionized water, and then the product was collected by centrifugation. The final product was dried in a vacuum oven at room temperature overnight.

Product Characterization. The crystal structure of the TiO_2 tubes was determined by X-ray powder diffraction (Philips PW3020) with Cu Kα radiation ($\lambda = 1.5418$ Å). The integration time was 2 h, and

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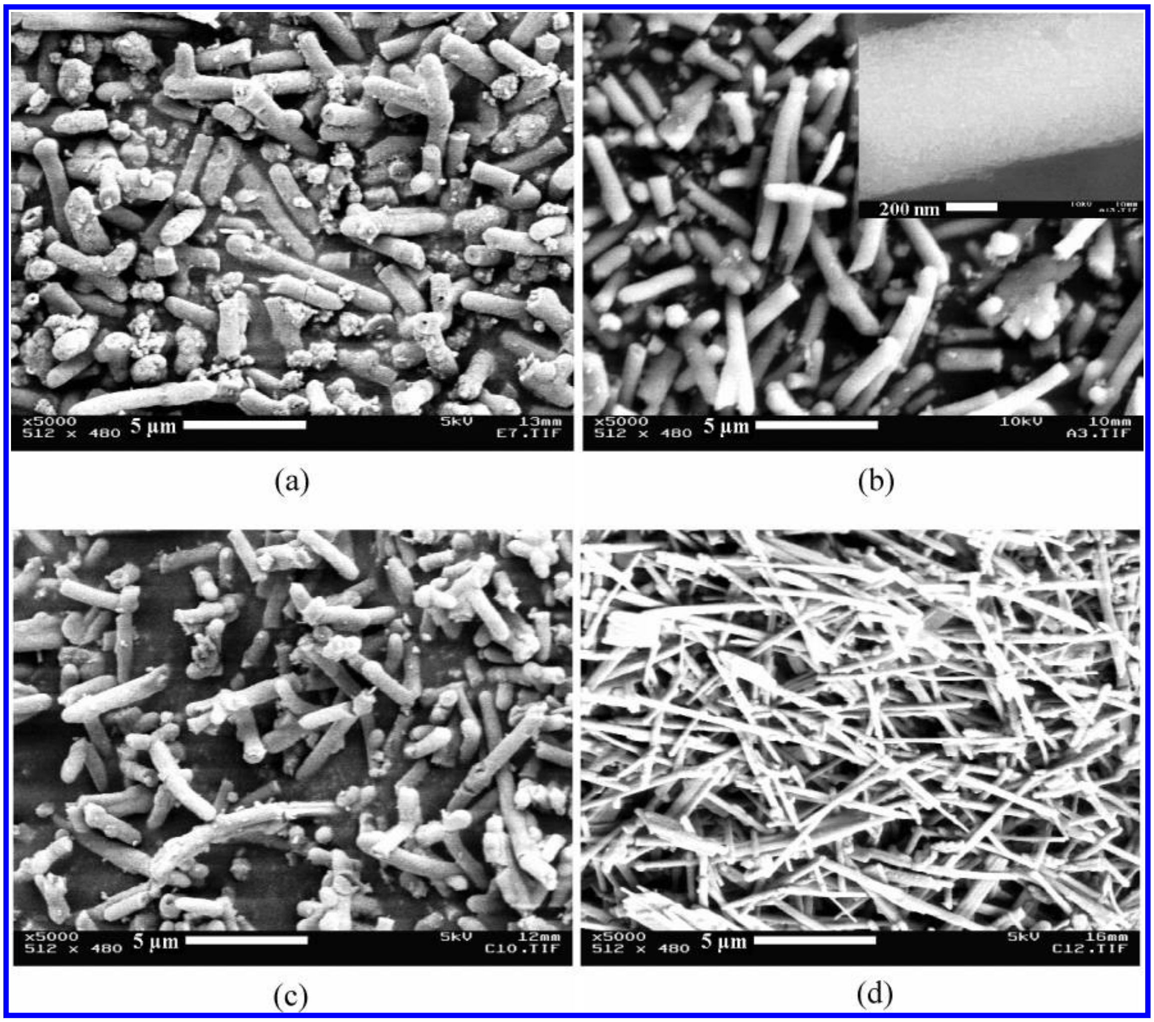

Figure 2. SEM images of as-synthesized titania−calcite composite rods with addition of CTAB = 20 mg, calcite = 20 mg, and different concentrations of titanium butoxide: (a) 0.15 mol/L, (b) 0.10 mol/L, (c) 0.05 mol/L, and (d) 0.01 mol/L. The typical addition rate is R = 0.865 mL/h. The inset SEM image in (b) shows the surface structure of an individual particle.

the step size was 0.02 deg/3 s. After the particles were coated with 80−100 nm of metal (Au 60%, Pd 40%), images of particle morphology and elemental analysis of the products were obtained using a scanning electron microscope (LEO 982 FE-SEM) equipped with an energy dispersive X-ray (EDX) spectrometer. TEM images were recorded on a JEOL TEM 2000 EX microscope at an accelerating voltage of 200 kV. The TEM sample was prepared by placing a drop of a dispersed solution of particles in hexane onto a carbon-coated copper grid and evaporating the hexane in a fume hood.

Results and Discussion

Parts a and b of Figure 1 show a representative SEM image and size distribution respectively of the rod-shaped calcite templates utilized in this study. The histogram in Figure 1b was determined by measuring approximately 75 particles by SEM and is based on the measured width (along the short axis) of the particles. The calcite particles are prismatic rods, with well-defined crystal faces. The width of the particles is in the range of 40−260 nm, and the average width is 89 nm. The calcite templates vary in length from several hundred nanometers to more than ten micrometers, but most of them are 2−5 μm long, so that the typical aspect ratio of the templates is 20−60 (histogram shown in Supporting Information). Parts a through d of Figure 2 show SEM images of the as-synthesized titania−calcite (shell−core) composites formed with decreasing concentrations of titanium(IV) *n*-butoxide added in the reaction. In Figure 2a−d, the concentration of titanium(IV) *n*-butoxide was 0.15, 0.10, 0.05, 0.01 mol/L, respectively. The titanium(IV) *n*-butoxide was dissolved in 10 mL of *n*-butanol before adding at 0.865 mL/h to the calcite suspension as described in the Experimental Section. The composites are cylindrical rods with widths that decrease as the concentration of titanium(IV) *n*-butoxide in the reaction is decreased and with lengths that are equivalent to the template particles. The inset image in Figure 2b shows the magnified particle surface structure. It can be seen that the surface is rough and composed of aggregated TiO$_2$ nanoparticles. Parts a−d of Figure 3 are the width distribution histograms of corresponding particles in Figure 2a−d. From Figure 3a−d, the width of the tubes is in the range of 400−970, 520−960, 290−880, and 150−450 nm, respectively. The average width is 796, 760, 619, and 271 nm respectively. The concentrations of titanium(IV) *n*-butoxide used in Figure 2a−d and 3a−d correspond to weight ratios of titanium(IV) *n*-butoxide/calcite of 75, 50, 25, 5, respectively. These results indicate that the thickness of the titania layer deposited on the calcite is controllable by simply varying the weight ratio of the TiO$_2$ precursor, titanium(IV) *n*-butoxide, to the template, calcite.

Following sol−gel synthesis to deposit the amorphous titania layer, the particles were calcined to sinter and crystallize the titania coating and then were exposed to acid to dissolve the calcite core and generate hollow TiO$_2$ tubes. Parts a−d of Figure 4 a−d show the SEM images of the tubes obtained from the

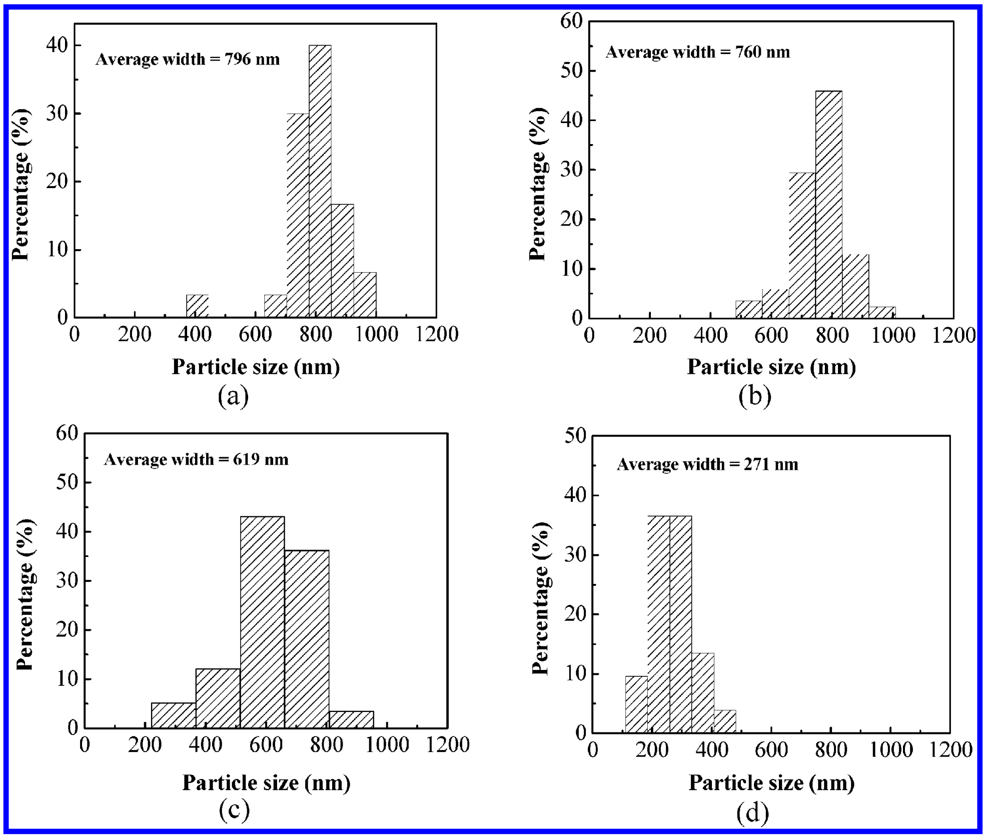

Figure 3. Particle width distributions of titania−calcite composites. (a−d) correspond to samples in Figure 2a−d.

composite rods shown in Figure 2a−d. The temperature during the sintering process was controlled at 550 °C. The particles have width and length distributions similar to those of the corresponding TiO_2/calcite rods and an open tubular structure. The corresponding TEM images of samples in Figure 4c,d are given in Figure 5a,b. The TEM images show low electron density regions that indicate the particles are hollow tubes. TEM observation of samples shown in Figure 4a,b was not feasible because of the thick shell of the tubes. The inset in Figure 4b shows the annealed surface structure. The shells of the tubes appear more dense and compact than the titania−calcite composites before sintering. The effect of sintering on the size and size distribution was examined by measuring particles by SEM. Parts a−d of Figure 6 show the particle width distributions corresponding to the samples shown in Figure 4a−d. From Figure 6a−d, the width of the tubes are in the range of 370−900, 480−750, 130−310, and 140 to 440 nm, respectively. The average width is 702, 639, 477, and 224 nm, respectively. Considering the tubular width is equivalent to the calcite template width, the average shell thickness of the tubes is 306, 275, 194, and 67 nm, respectively. In every sample, the width of the hollow tubes is reduced in comparison to the calcite−titania core−shell precursor particles. Comparison of the average width of the core−shell rods with the average width of the resulting hollow tubes shows that the widths of the tubes in Figure 6a−d are 88%, 84%, 77%, and 83%, respectively, of the width of the core−shell particles that they were formed from. Shrinkage during the sintering process results in the densely packed TiO_2 structure. A close examination of the samples shown in Figure 4a−d shows that some tubes have one end or both ends closed when the TiO_2 coating is thick, such as the samples in Figure 4a,b. With thinner TiO_2 coatings, such as those for particles in Figure 4d, most of the tubes appear open on both ends.

The elemental composition of the prepared calcite−titania core−shell nanorods and the titania tubes were verified with EDX spectroscopy, as shown in Figure 7. The EDX spectra (7a) are of the core−shell rods and are composed of Ti, O, and Ca peaks, indicating the presence of TiO_2 and calcite. The EDX spectra (7b) are of the tubes and show the intensity of the Ca peak decreasing significantly, confirming the removal of calcite. The small Ca peak that remains is likely from a small quantity of Ca adsorbed on the surface of TiO_2 due to the high surface energy of bare TiO_2.[11,38] The C and Au peaks are from the carbon tape and Au coating used for SEM characterization.

To further our understanding of sol−gel coating against calcite templates, we conducted a series of experiments to investigate the influence of various experimental parameters on the particle formation. In this series of experiments, the experimental conditions used for synthesis of particles in Figure 2b were used as the base case for comparison. Individual experimental variables were changed, and the effects of changing these variables were investigated by comparing the product to that obtained with the standard conditions. The goal was to better understand the particle growth mechanism so that this synthetic technique may be applied to the sol−gel synthesis of tubes of other materials.

To confirm that the rod-shaped calcite particles are responsible for titania tube formation, a control experiment was carried out without calcite particles. As expected, the TiO_2 forms as nanoparticles that then aggregate into larger particles with no tubes present (Figure 8a). The calcite particles thus act as true templates and the surface growth of titania on calcite is a requirement for tube formation.

A control experiment without the CTAB was conducted to investigate the role of surfactant, and the product is shown in Figure 8b. The rod-shaped particles appear irregular with rough surfaces when CTAB is omitted from the synthesis. In comparison, Figure 2b shows that CTAB allows for growth of a smoother,

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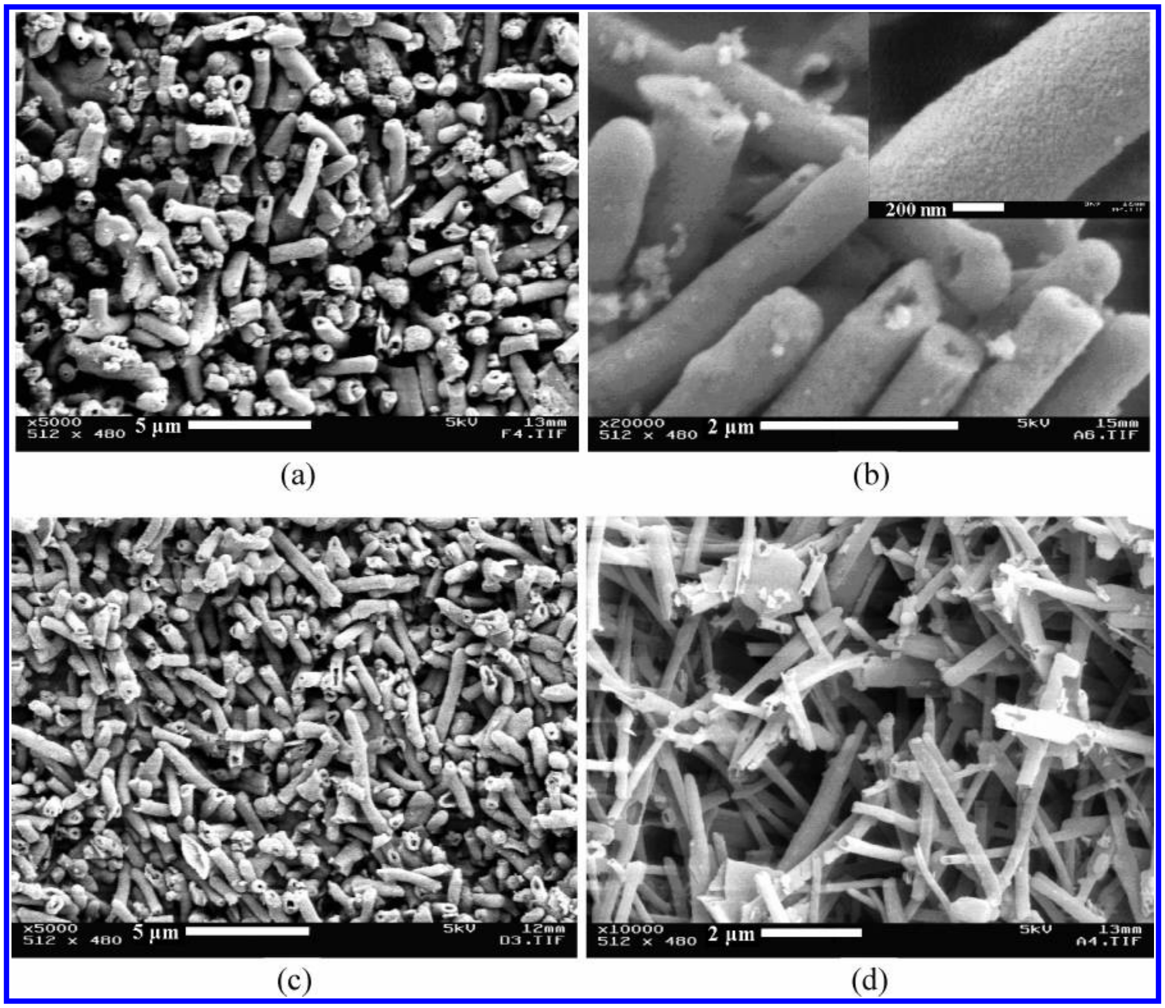

Figure 4. SEM images showing width-tunable titania tubes after calcinations and acid etching to remove the calcite core from products shown in Figure 2a−d. The width of the tubes decreases with decreasing concentration of titanium(IV) *n*-butoxide reactant. The inset SEM image in (b) shows the surface structure of an individual titania tube.

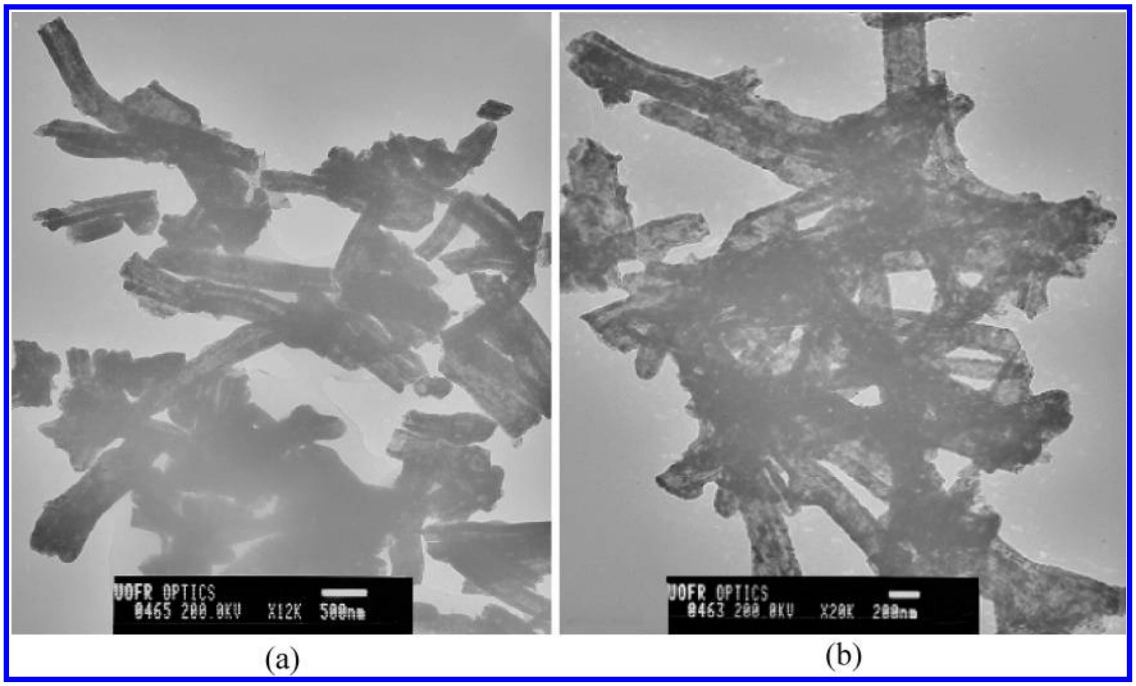

Figure 5. TEM images of the as-prepared titania tubes. (a, b) correspond to samples in Figure 4c,d, respectively.

uniform titania shell. The cationic CTAB is attracted to the negatively charged (110) crystal faces of calcite.[37] Since titania is also negatively charged,[39] the CTAB should also adsorb onto the titania precursors that initially form in solution. The adsorbed

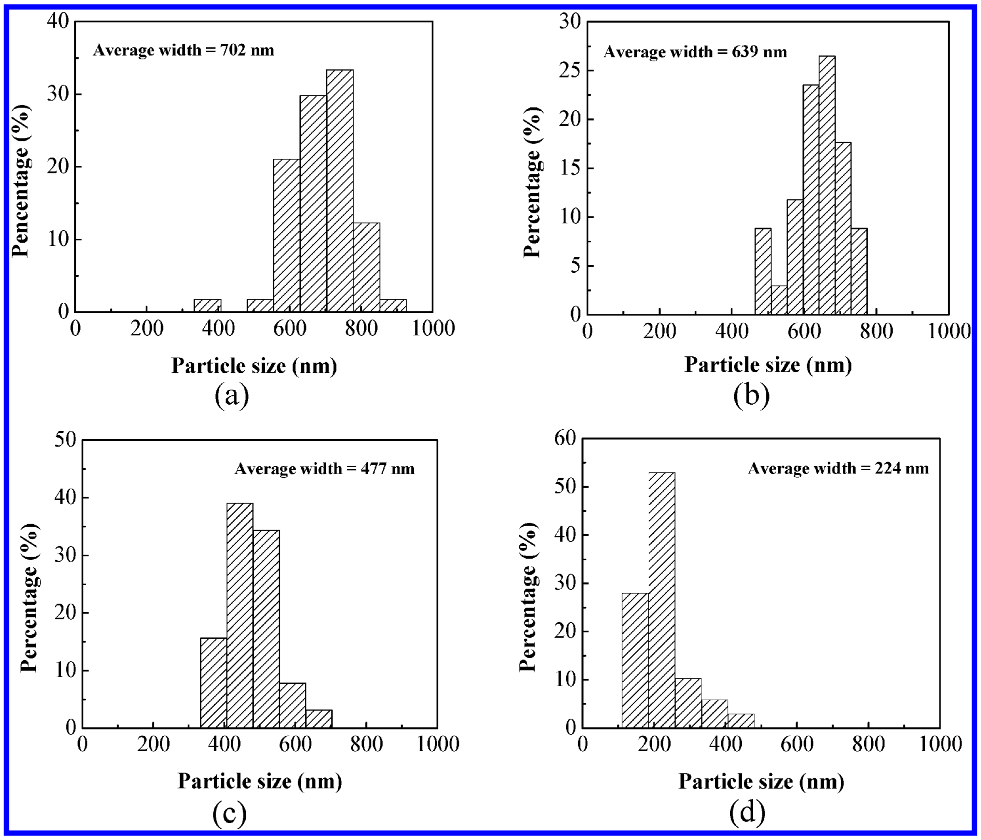

Figure 6. Particles width distributions of titania tubes. (a−d) correspond to samples in Figure 4a−d.

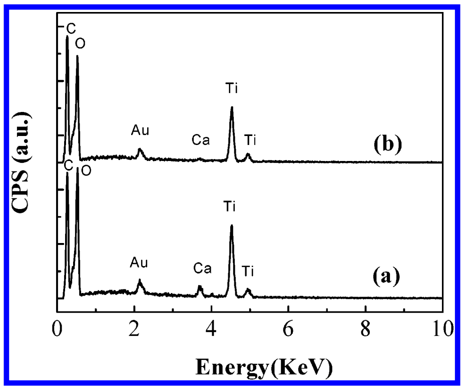

Figure 7. EDX spectra of (a) titania−calcite composite rods as synthesized and (b) titania tubes after calcination and acid-etching posttreatments.

CTAB should reduce electrostatic repulsion between titania and calcite, facilitating the coating of the calcite surface with titania and the eventual formation of a titania shell of controlled thickness. Without the addition of CTAB, the TiO_2 precursor does not attach to the calcite surface easily so that a uniform and smooth shell does not form. Electrostatic attraction has been widely used to form core−shell structures by assembling oppositely charged species, including creating TiO_2 and SiO_2 shells on positively charged templates.[40−42] The present example is different in that titania growth on a like-charged template is mediated by the oppositely charged surfactant. The data indicate that the titania shell initially forms on the longest sides of the calcite rods, since calcite coated with thin titania shells have open ends and the ends become closed as the shell thickness is increased. It therefore appears that titania preferentially grows on the long axes of the calcite crystals. Our previous study of the synthesis of rod-shaped calcite shows that the longest axes of the calcite crystals have (110) crystal faces exposed.[37] The surfactant CTAB preferentially adsorbs on the (110) face, and preferential surfactant adsorption appears to be a critical factor in directing the growth of titania as tubes. The requirement of the presence of CTAB in the TiO_2 tube formation was further verified by control experiments in which CTAB was replaced with the nonionic surfactant octylphenoxypolyethoxyethanol (Triton X-100) and anionic surfactant docusate sodium (AOT) during the TiO_2 formation. The results (Supporting Information) show that TiO_2 did not coat the calcite cores when the anionic and nonionic surfactants were used.

It has been reported that slow addition of reagents during sol−gel synthesis of silica gives the hydrolyzed molecular precursor enough time to diffuse to seed particles so that secondary nucleation of silica can be effectively avoided and silica grows only onto seed particles.[43] Due to the similarity between the sol−gel synthesis of silica and titania, we employed the same slow addition approach to facilitate growth of titania on the calcite seed particles. To verify this effect, we carried out a control experiment with simple mixing of all of reactants together at one time. Adding a large quantity of titanium(IV) *n*-butoxide at the start of the reaction results in a significant fraction of the hydrolyzed TiO_2 precursors forming in solution at the early stages of the reaction. The titania particles that nucleated in solution can continue to grow, or be adsorbed or react with the growing titania shell on the surface of the calcite particles. As a result, the titania shell that forms on the calcite particles is very irregular and nonuniform, as shown in Figure 8c. A well-defined shell is

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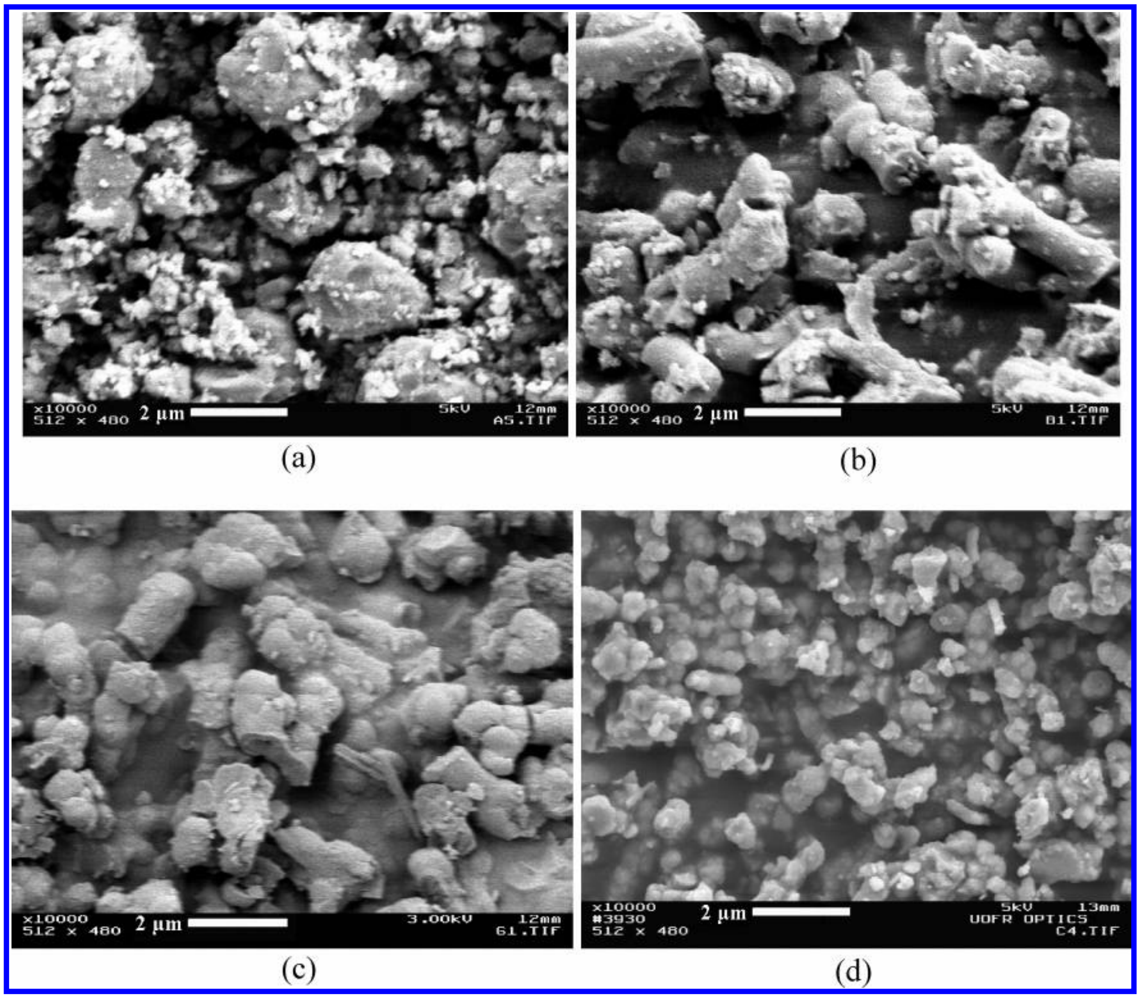

Figure 8. Influences of altering single reaction parameters on the formation of titania−calcite rods: (a) calcite template omitted, (b) CTAB surfactant omitted, (c) mixing of all reagents at the start of the reaction instead of slow addition of titanium source, and (d) result with added NH$_4$OH catalyst.

difficult to form without slow addition of reagents that enables controlled growth of titania on the calcite surface.

Previous studies reported that the synthesis of TiO$_2$-coated composites requires the presence of a catalyst, such as NH$_4$OH.[35,44] For the calcite templates, however, the addition of NH$_4$OH prevents the formation of composite particles. Figure 8d shows SEM images of the product when TiO$_2$ was synthesized with 0.7 mL of 28−30 wt % ammonia solution added. The reactant composition is the same as that of the standard composition except for the presence of 0.2 g of ammonia from the added ammonia solution. With the catalyst present, TiO$_2$ grows into irregular aggregates instead of forming a shell around the calcite templates. Titanium(IV) alkoxides are highly reactive so that the hydrolysis rate is fast.[39,45] The presence of the catalyst accelerates the hydrolysis further. As the alkoxide is hydrolyzed, TiO$_2$ precursors form that condense into oxopolymers and are eventually transformed into an oxide network. The rapid hydrolysis in the presence of catalyst causes the TiO$_2$ precursors to condense into gels before they have enough time to adsorb to the calcite template surface. On the other hand, slow hydrolysis in the absence of catalyst allows the hydrolyzed precursors to diffuse to the oxopolymer network forming at the surface of the templates, allowing controlled growth of the shell.

The as-prepared amorphous titania shell can be crystallized to rutile or anatase phases by sintering the composite particles.

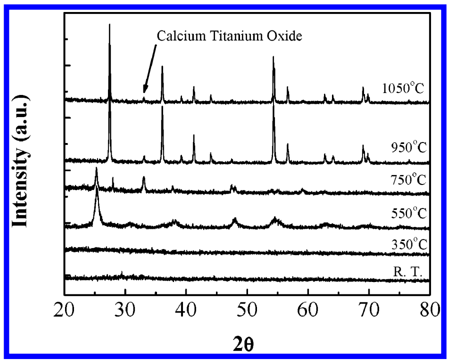

Figure 9. XRD patterns of synthesized products showing the formation of various phases at different sintering temperatures: amorphous titania and calcite under room temperature (R. T.); amorphous titania at 350 °C; anatase titania at 550 °C; mixture of anatase and rutile titania at 750 °C; rutile titania at 950 °C and 1050 °C.

Crystalline titania tubes are then obtained by acid etching to remove the calcite core. Figure 9 shows the XRD spectra of the product as a function of sintering temperature. The as-synthesized particles are composed of amorphous TiO$_2$ and calcite crystals, with the diffraction peak of $2\theta = 29.44°$ assigned to calcite (104) (JCPDS File No. 86-0174). After sintering at 350 °C and acid etching, there is only the amorphous TiO$_2$. When the sintering temperature is increased to 550 °C, amorphous TiO$_2$ crystallizes to the anatase phase (JCPDS File No. 84-1286). Titania obtained

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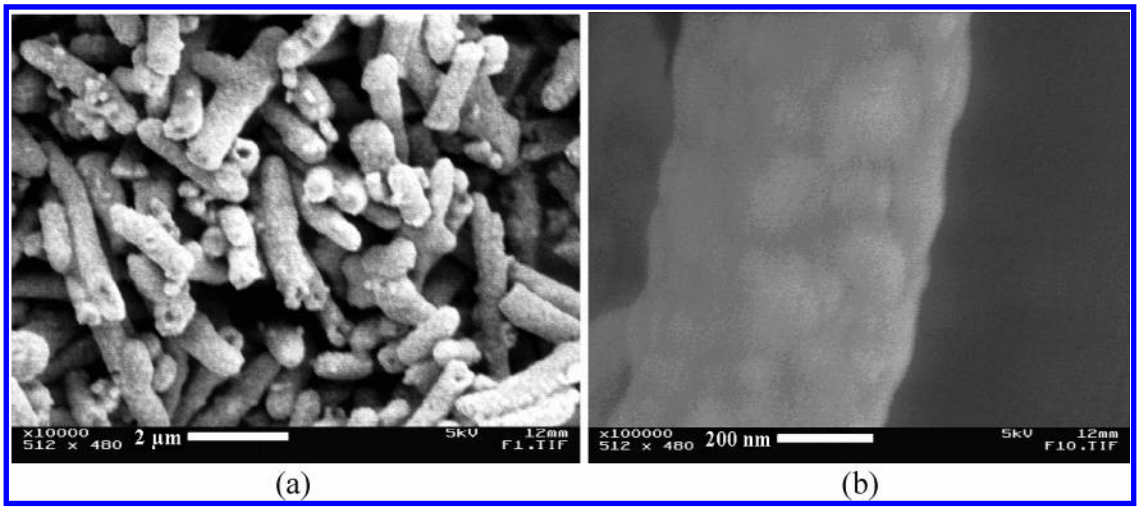
(45) Jiang, X.; Herricks, T.; Xia, Y. *Adv. Mater.* **2003**, *15*, 1205.



(a) (b)

Figure 10. (a) TiO_2 tubes calcined at 950 °C and (b) the surface of an individual tube. These particles were obtained by further treatment of particles shown in Figure 2b.

after sintering at 950 °C has the rutile crystalline phase (JCPDS File No. 84-0514). From the XRD pattern, the phase transitions from amorphous to anatase and from anatase to rutile occur respectively around 450 °C and 650 °C, which is consistent with previous studies.[29] A new diffraction peak ($2\theta = 33°$) appears when the sintering temperature is above 650 °C, and the new peak can be indexed to the (0 0 10) plane of calcium titanium oxide (JCPDS, File No. 14-0152). The existence of this peak suggests that some crystalline titanium calcium oxide forms at high temperature due to incomplete removal of the calcium by acid etching. The XRD results are also consistent with the EDX spectra in Figure 7 that show a small amount of calcium remaining after etching.

Previous studies have shown that high-temperature sintering disrupts the tubular structure of TiO_2 tubes due to crystal grain growth and densification.[20,29] However, in this study, TiO_2 tubes maintain their tubular structure after annealing. Figure 10a shows the morphology of TiO_2 tubes obtained after annealing the particles (shown in Figure 2b) at 950 °C for 2 h and removing calcite by acid etching. It is apparent that the tubular structure is maintained. Figure 10b shows the surface of the tubes after annealing. The surface consists of many protrusions of rutile TiO_2 crystallites. Previous studies of titania tubes dealt with much smaller tube dimensions than those in the present study. The larger tube structure is less likely to be disrupted by the small crystallites that form during annealing. The calcite core also supports the titania and helps to maintain the tubular structure during high-temperature treatment. Attempts to remove the calcite before high-temperature sintering failed because the amorphous TiO_2 shell and calcite core were both dissolved in 1 M HCl acid solution. The ability to control titania size and crystal structure are important for application in photocatalysis, photovoltaics, or as hydrophilic fillers in fuel cell membranes. For example, the as-fabricated anatase TiO_2 tubes show UV−vis absorption spectra (shown in the Supporting Information) that are tunable by varying the tube wall thickness. The controllable optical properties may be useful for application of the titania tubes in photocatalysis and photovoltaics.

On the basis of the above experimental results and analysis, we can formulate a possible growth mechanism for the titania tubes. The calcite particles are first dispersed in *n*-butanol, and the cationic surfactant CTAB is added and adsorbed onto the surface of the particles. To start the sol−gel reaction, titanium(IV) *n*-butoxide is added slowly with a syringe pump. The titanium(IV) *n*-butoxide reacts through hydrolysis and polycondensation to form the oxopolymers that are then transformed into an oxide network of TiO_2. The absence of catalyst effectively slows the hydrolysis rate, which is essential to control the formation of homogeneous titanium oxide networks. Slow addition of titanium(IV) *n*-butoxide allows time for the initial hydrolysis products to diffuse to the calcite surface. Secondary growth of titania in solution is thus minimized so that TiO_2 grows as a layer of controllable thickness on the calcite surface through condensation reactions. Titania initially forms on the longest sides of the calcite because of the preferential adsorption of CTAB on the (110) crystal faces. As a result, titania tubes form with open ends when the amount of titanium(IV) *n*-butoxide added is low. When more titanium precursor is added, the TiO_2 layer eventually grows over the ends of the calcite particles so that TiO_2 tubes are generated with one or both ends closed. Subsequent sintering transforms the amorphous phase to anatase or rutile titania, depending on the temperature. Finally acid etching dissolves the calcite core leaving hollow TiO_2 tubes. This formulated fabrication approach can be applicable to other oxide materials synthesized via sol−gel chemistry. Silica tubes have been synthesized in our laboratory through the same process by growing silica around the calcite rods, then dissolving the calcite core in acid, as shown in the Supporting Information.

The broader applications of the fabrication procedure may be improved by producing size-monodisperse tubes. The data show that the size distribution of the tubes is determined by the size distribution of the calcite template particles. Future research on reducing the size distribution of the calcite templates will allow monodisperse tubes to be synthesized. Microemulsion-based synthesis of calcite may be optimized to produce monodisperse calcite crystals and as a result narrow the size distribution of the templated TiO_2 tubes. The as-synthesized TiO_2 tubes may also be fractionated to improve the particle size distribution. For example, applied electric fields can be used to separate different sized TiO_2 tubes since the eletrokinetic response of particles to the applied field depends on their size and shape. Various colloid particles and biological cells have been separated and sorted under an electric field.[46] Also, filtration or centrifugation processes can also be used to separate different sized TiO_2 tubes.

Conclusions

Novel titania tubes with tunable wall thickness were synthesized from the sol−gel reaction of titanium(IV) *n*-butoxide by

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(46) Morgan, H.; Green, N. G. *AC Electrokinetics: Colloids and Nanoparticles*; Research Studies Press, Ltd.: Hertfordshire, 2003.

templating against rod-shaped calcite particles. The resulting core−shell composite rod-shaped particles were converted to tubes by sintering followed by acid etching to remove the calcite core. The amorphous titania shell deposited on calcite can be crystallized to the anatase or rutile phase by varying the sintering temperature. Although some reduction in particle width occurs during the sintering and etching processes, the titania tubes maintain their tubular structure after crystallization. The average width of the prepared titania tubes ranges from 200 to 700 nanometers by varying the weight ratios of titanium(IV) *n*-butoxide/calcite used in the synthesis from 5 to 75. The width was shown to increase with increasing quantity of titania precursor. A series of control experiments were conducted to investigate the influence of several reaction parameters on the titania tube formation and growth processes. The experimental results suggest a possible growth mechanism of the titania tubes. The cationic surfactant CTAB enhances deposition of amorphous titania onto calcite by reducing electrostatic repulsion between calcite and titania. The thickness and uniformity of the titania shell was adjustable by controlling the reaction and deposition rates through the slow addition of reagents in the absence of catalysts.

The ability to control titania size and crystal structure are important for application in photocatalysis, photovoltaics, or as hydrophilic fillers in fuel cell membranes. For example, the as-fabricated TiO_2 tubes show a tunable UV−vis absorption spectra (shown in the Supporting Information) with tunable wall thickness. The controllable optical properties may be useful for application of the titania tubes in photocatalysis and photovoltaics. The fabrication approach may be applicable to other oxide materials synthesized via sol−gel chemistry. Silica tubes have been synthesized in our laboratory through the same process by growing silica around the calcite rods, then dissolving the calcite core in acid, as shown in the Supporting Information. The broader applications of the fabrication procedure may be improved by producing size-monodisperse tubes. The data show that the size distribution of the tubes is determined by the size distribution of the calcite template particles. Future research on reducing the size distribution of the calcite templates will allow monodisperse tubes to be synthesized.

Acknowledgment. We acknowledge support of this research from the DOE (DE-FG02-05ER15722) and the DOE through the Laboratory for Laser Energetics (DE-FC03-92SF19460). The electron microscopy facility at the University of Rochester is supported by NSF CTS-6571042. We thank for Prof. S. J. Burns and C. Pratt for useful discussion and their help with the XRD measurement.

Supporting Information Available: Histogram of length distribution along the long-axis direction of calcite templates employed for synthesis of titania tubes; XRD to check for mesoporosity from CTAB; XRD at different rates of addition of reagents; effect of surfactants on the formed TiO_2/calcite rods. This material is available free of charge via the Internet at http://pubs.acs.org.

LA701335J