Published in final edited form as:

Small. 2012 December 7; 8(23): 3691–3697. doi:10.1002/sml.201200421.

Biotemplated Synthesis of Hollow Double-Layered Core/Shell Titania/Silica Nanotubes under Ambient Conditions

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Abstract

Bacterial flagella, protein nanotubes (~15 nm wide) detached from *Salmonella typhimurium* bacteria, are used to template the formation of titania/silica core/shell double-layered nanotubes in aqueous solution under ambient conditions through a sol–gel process. The thickness of each layer is tunable by varying the concentration of precursor solutions or reaction times. Upon heating, the flagella can be removed and the inner titania layer can be transformed into a nanocrystalline layer supported by the outer silica sheath. Nanotubes with different inner pore diameters and morphologies could be templated by other bionanofibers such as M13 phage and bacterial pili. This work shows that bionanofibers can be used as a universal biotemplate for the green synthesis of nanotubes with tunable wall thicknesses.

1. Introduction

Nanostructural titanium oxide (titania, TiO_2) nanotubes are one of the most widely studied materials because of their unique and excellent properties. Titania is chemically stable, non-toxic and well known as a wide gap semiconductor oxide. It also has high photocatalytic activity under UV irradiation but not visible light. Titania nanotubes have a variety of applications as chemical sensing devices, dye-sensitized solar cells, gas sensors, electrodes of solar cells, and photocatalysts.^[1–4] They are also very promising for biomedical applications, such as tissue engineering, biosensing, and drug delivery, due to their chemical stability and non-toxic characteristics.^[5–9] There are two general methods for the synthesis of titania nanotubes: one is through the self-assembly of titanium oxide during chemical synthesis processes such as the well-known ‘anodic oxidation’;^[2,4] the other one is through the use of a filamentous nanostructure as a template.^[10] The morphology and size of the nanotubes usually depend on the type of template materials in the templating approach. A liquid-phase deposition method has been widely used to coat titania on the templates. After deposition, usually, the templates can be removed chemically or physically to generate hollow nanotubes. In recent years, biological systems have been used as supporting templates or catalysts to synthesize nanoscale titania materials and nanotubes.^[11–19] Biological systems are very easy to scale up and the biological templates can be easily removed under ambient conditions or by heat treatment. They also exhibit precise control over morphology, size distribution and their spatial arrangement. Moreover, some biological templates can self-assemble into highly ordered structures, which are a critical property for

materials to be used in nanofabrication and nanotechnology.^[20–22] To date, there are a variety of bio-enabled titania nanoparticles and nanotubes which have been synthesized using proteins such as silicatein, silaffins, positively charged lysozymes and peptides.^[11,13,14,17,19,20,23] These proteins are used as enzymatic biocatalysts during titania deposition process. Consequently, this approach is limited to the availability of the specific templates. Tobacco mosaic virus or lipids have been reported as bio-inspired templates for titania synthesis.^[15,18] However, special techniques with multiple steps have to be employed, preventing their practical applications.

Due to the excellent photoactivity of titania, in most cases, the materials used to support titania materials are etched or degraded, which considerably limit their practical applications. However, as one of photo-catalytically inactive substances, silica has been used to encapsulate titania to fabricate double layered, core/shell structured, and hybrid materials.^[24–26] Furthermore, due to UV transparent property, thin shielding layer of silica (20 nm in thickness) on the titania film can improve the photo-catalytic activity toward photo oxidation of polystyrene.^[24] Another approach to improving the photo-catalytic activity of titania film is to use mesoporous silica as a matrix where titania nanocrystals are dispersed. Such structure exhibits a large surface area, which exposes more active sites of titania.^[27] Therefore, making titania/silica double-layered nanotubes would be an alternative attractive approach.

Toward this goal, we employed bacterial flagella as templates for the synthesis of titania nanotubes in aqueous solution under mild conditions. Then, silica was deposited on surfaces of titania as the second layer, resulting in the formation of double-layered nanotubes with uniform diameter. Bacterial flagellum can be pictured as a nanofiber polymerized from only proteins called flagellin (*FlhC*). It has a hollow helical structure with 11 *FlhC* monomers assembled per 2 turns. The outer diameter of the flagella filament varies from 12 nm to 25 nm depending on the species of bacteria. Their length can be up to 10–15 μm , depending on the number of monomers.^[28] Recently, we demonstrated the fabrication of silica nanotubes using genetically modified flagella as a template.^[29] Here, we also adopt an environmentally friendly aqueous sol-gel process to deposit titania on flagella templates, followed by silica, getting titania/silica double-layered nanotubes with controlled size and morphology. After calcification, the flagella templates could be removed. Amorphous titania was transformed into crystalline nanoparticles (anatase phase) and dispersed close to the central tunnel of nanotubes. At the same time, the silica sheath prevented collapse of inner titania layer as supporting matrix (Scheme 1).

2. Results and Discussion

Titania nanotube array could be chemically synthesized directly.^[2,4] Templated synthesis of titania nanotubes using sol-gel process is another promising approach which gives us more freedom.^[15,30] The hydrolysis precursors, such as titanium isopropoxide and titanium butoxide, were usually performed in organic solvents.^[30,31] It is well-known that most of the bio-enabled templates cannot survive in organic solvents. As a matter of fact, we also confirmed free flagella tended to be totally depolymerized in pure ethanol solution (data not shown). Alternative routes have been developed, such as immobilizing the templates on substrates^[18,30] or carrying out the reaction at very low temperatures,^[15] but limited their practical applications. In this work, we developed a new sol-gel method for the synthesis of titania nanotubes. The reaction was carried out in aqueous solution, close to room temperature and neutral pH value. 3-aminopropyltriethoxysilane (APTES) was used as the initial nuclei followed by the subsequent titania deposition. Silica as the second layer was then coated following our previous description.^[29]

High concentration of flagella were isolated from *Salmonella typhimurium* by high speed vortexing.^[32] It is a simple and easy way to produce a large amount of flagella with high purity. After coated the first layer of titania on flagella templates, the titania/flagella composites were characterized using scanning electron microscopy (SEM) (Figure 1A). A continuous layer of amorphous titania with rough surfaces totally covered on the surface of flagella. The nanotubes kept the characteristic curly morphology of flagella. We propose that the positively charged APTES adsorbed onto the flagella surface by hydrogen bonding or electrostatic interaction.^[29] The ζ potential of wild type flagella is about -6 mv, indicating the presence of negative charges on the flagella surface. Partially hydrolyzed APTES formed silicic acid as nuclei to mediate the formation of titania nanotubes. Energy dispersive X-ray (EDX) analysis indicated that the amorphous layer is composed mainly of titanium with minor silicon (Figure 1B). The silica portion should come from the hydrolysis of APTES. The addition of a silica layer increased the diameter of the nanotubes and amplified the roughness of the titania layer (Figure 1C). The formation of silica layer can be confirmed by EDX (Figure 1D). Because the titania layer was covered by the silica layer, the relative ratio of titania to silica significantly decreased.

Titania nanotubes were also characterized by TEM as shown in Figure 2. After coating with the titania layer, the nanotubes exhibited very rough surfaces unlike the flagella based silica nanotubes which acquired pearl-necklace-like surface features.^[29] The diameter of the titania nanotubes ranges from 30 to 80 nm. Compared to flagella based silica nanotubes in our earlier work,^[29] the titania nanotubes appear more “sticky” and some excess titania is nucleated at the crossover sites between nanotubes (Figure 2A,B). This may be ascribed to the low density of titania prepared by the sol-gel method.^[33] Titania nanotubes are not like silica nanotubes in that after being coated with amorphous titania, the flagella projected pore at the center of the nanotubes was present but barely observable (Figure 2C, marked by arrows). Interestingly, after the titania nanotubes were coated by the silica layer, a uniform pore size with a diameter of about 15 nm became visible (Figure 3A). It should be noted that flagella had a uniform diameter of ~ 15 nm under TEM according to our previous research.^[29] The high density of silica might enhance the contrast between flagella templates and inorganics. Moreover, the titania prepared by sol-gel method has a tenuous structure and allows silica precursors to penetrate inside the very open network.^[34] The diameter of titania/silica double-layered nanotubes increased to 40–90 nm. Meanwhile, the thickness of titania or silica layer is controllable by changing amount and concentration of the precursor solution and/or reaction times. After being coated by less titania (half of original precursor solution) and more silica (double of original precursor solution), the nanotubes became more flat with some free silica nanoparticles nucleated or hanging on the surfaces (Figure 3B, left). If coated with less silica (half of original precursor solution) and more titania (double of original precursor solution), the nanotubes exhibited rougher surfaces and the central tunnels became invisible (Figure 3B, right).

Different morphologies of titania nanotubes can be obtained using other biotemplates. Here, the filamentous M13 bacteriophage (~ 900 nm long and 7 nm wide), a virus that specifically infects bacteria,^[35,36] and bacterial pili ($1\text{--}2$ μm long and ~ 7 nm wide), tiny nanotubes attached to bacterial cells to assist their adhesion to solid surface,^[37] were used as bio-inspired templates for the synthesis of titania nanotubes. Using the same conditions on flagella, both phage and pili were successfully coated by amorphous titania (Figure S1, Supporting Information (SI)). Because the natural morphologies of phage and pili are quite different than that of flagella, titania nanotubes based on phage and pili exhibited obvious morphological differences. Titania nanotubes on the phage template showed some random coils and curves; however, pili based titania nanotubes exhibited straight morphology. These facts suggest that the method we used can be extended to other biological templates with different morphologies which may broaden their applications. From this work, a general

procedure can be developed for coating titania on bio-enabled templates and/or other templates that cannot survive in organic solvent.

After flagella were coated by titania, the samples were washed several times with water and ethanol and dissolved in ethanol. Then the samples were air dried and annealed at 150 °C and 200 °C, respectively, for 2 h (Figure 4). At 150 °C, the organic flagella templates start to decompose revealing hollow nanotubes composed of a thin layer of titania with the curly morphology of flagella (Figure 4A). The outer diameters of the nanotubes decreased to 40–60 nm with a wall thickness of 10–25 nm and an inner diameter of 20–35 nm. At higher temperature (200 °C), the titania nanotubes began to collapse and the characteristic template morphology disappeared. Much shorter but thicker straight nanotubes with corrugated surfaces were observed (Figure 4B). A previous study also confirmed that at high temperatures (200 °C and 400 °C), the amorphous titania nanotubes were severely shrunk.^[10] Interestingly, when we subjected the nanotubes to heat treatment at 200 °C for 2 h after coating with a very thin layer of silica (tenth of original tetraethyl orthosilicate (TEOS) concentration), most of the nanotubes remained intact with a pore size fitting the diameter of flagella (Figure 4C). This data demonstrated the ability of silica as “skeleton” supporting the inner layer of titania and preventing titania nanotubes from collapse. There were still some nanotubes with a larger pore size because the silica layer on the surface of some flagella was either nonexistent or too thin to preserve the nanotubes (Figure 4C, as marked by arrows).

After being coated with the second silica layer, the double-layered titania/silica nanotubes were calcined at different temperatures (500 °C, 800 °C) to remove the organic template under air in a tube furnace (Figure 5). TEM images of the titania/silica nanotubes calcined at 500 °C showed hollow structures with a uniform pore size of 10 ± 0.5 nm but with very rough outer surfaces. The open-ended tubular structures exhibit an outer diameter of 30–80 nm with a wall thickness of 10–60 nm (Figure 5A). The selected area electron diffraction (SAED) pattern clearly indicated the characteristic crystallographic (101) and (004) planes of the anatase phase (Figure 5A, inset). When the calcination temperature was increased to 800 °C, some of the nanotubes broke into shorter fragments. The diameter of the pore decreased to 8 ± 0.5 nm. The outer diameters also decreased to 25–50 nm (Figure 5B). However, the thicker layer of silica improved the integrity of titania/silica nanotubes at high temperature (Figure S2, SI). This result also demonstrates that the silica shield has high thermal stability and can support the inner titania layer as a “skeleton”. After dried at 40 °C for overnight, the samples were further analyzed by thermal gravimetric analysis (TGA) to evaluate the removal of flagella template (Figure S3, SI). The weight-loss below 150 °C is primarily related to the evaporation of free and adsorbed water and residual solvent. The decomposition of flagella templates is mainly located in the region from 150 to 560 °C (Figure S3A, SI). After the flagella were coated with titania and silica, the decomposition of titania and silica bonded groups such as –OH and/or unhydrolyzed –OR occurs at the region from 420 to 600 °C^[38] in addition to the decomposition of flagella templates (Figure S3B, SI).

In order to determine whether the titania still existed inside the silica sheath after calcination at high temperature, the double-layered of titania/silica nanotubes was analyzed by energy dispersive x-ray spectroscopy (EDX) (Figure 6). Here, thicker layer of silica was coated (double concentration of original TEOS) for EDX analysis in order to fit the selected sites on and off the axis of nanotubes. It clearly showed that the marginal sides of the nanotubes are only composed of silica. In the center, both titania and silica were detected, indicating the presence of a titania layer inside the silica layer. Before calcination, we found a very similar pattern of titania/silica distributions (Figure S4). Many reports confirmed that amorphous titania starts phase transitions upon heating. Yang et al. reported the amorphous

titania nanotubes start to initiate a phase transition to crystals in the anatase and rutile phases at 300 °C and 500 °C, respectively.^[39] Polycrystal-line anatase phase of the titania nanotubes prepared by sol-gel method was obtained after being calcinated at 650 °C for 2 h.^[40] In this work, the phase transition of titania/silica double-layered nanotubes was investigated by high resolution transmission electron microscopy (HRTEM) (Figure 7). Figure 7A showed the morphology of the titania/silica nanotubes annealed at 500 °C for 4 h. The outer diameters of the nanotubes with rough surfaces were not very uniform. However, the inner pore created by removing the flagella template was very smooth and the diameter was consistent with flagella size. Higher magnification of the TEM images showed some dark small clusters well dispersed in an amorphous background and close to the center pore (Figure 7B). These small clusters should be the crystalline titania nanoparticles converted from amorphous titania upon heating.^[34] The diameters of the nanoparticles range from 2 to 8 nm. Furthermore, at high resolution, polycrystalline nanoparticles could be clearly observed with identical lattice fringes ($d = 0.35$ nm) corresponding to the d-spacing between adjacent (101) crystallographic planes of anatase titania phase (Figure 7C,D marked in the dash line cycles). At the same time, these titania nanoparticles are close to the center pore (as marked by dash line) of the nanotubes. SAED analysis also confirmed the characteristic crystallographic (101) and (004) planes of the anatase (Figure 7C, inset). This data indicated that, after calcination at 500 °C, the amorphous titania was transformed into the crystalline anatase phase. In the meantime, the crystalline titania nanoparticles were embedded inside the silica supporting matrix. Actually, the first layer of titania has a tenuous structure with the very open network,^[34] which allows silica to penetrate into the titania layer, forming a mixed composition at the interface between the first titania and the second silica layer. During calcination, the silica penetrated inside titania layer can support the titania nanoparticles and prevent their further collapse. In this process, the silica sheath still remained to be amorphous because it was only transformed into crystalline phase when the temperature reached up to 950 °C.^[29]

Due to its excellent photocatalytic and photovoltaic properties, titania has already shown great promise in many areas such as solar energy harvesting, air cleaning, and water purification.^[24–27] Because titania nanoparticles aggregated spontaneously in the reaction system, resulting in a rapid loss of their photocatalytic activity, alternative approaches have been developed such as dispersing titania nanoparticles in porous solids or immobilizing them on the inert surfaces.^[41,42] In this work, the titania nanoparticles were successfully wrapped inside silica matrix. The photocatalytic activity may be decreased due to the outer silica layer, which may block some of the active sites of titania.^[41] However, the silica sheath of hollow nanotubes is only 10 to 60 nm in thickness (Figure 5A) and it is UV transparent. Furthermore, after the removal of the flagella template, the central pore, which is mainly composed of titania nanoparticles, became surface-exposed. An alternative method to maintain the active sites of titania is to coat the silica surface with a titania layer. We have also demonstrated that a titania layer could be coated on silica nanotube templated on flagella (Figure S5).

The advantage of our flagella-templated approach for the synthesis of the double-layered titania/silica nanotubes can be summarized as follows: A) The outer silica layer with the silane group is easily modifiable. For example, in waste water treatment, the nanotube surfaces can be converted to hydrophobic interface which minimize competition between water and organics; B) The silica coating protects titania particles from abrasive interactions with substrates; C) The thickness of titania or silica layers is tunable by varying the precursor concentrations or reaction time; D) The central pore provides a “void space”^[34] that could facilitate photocatalytic activity; E) After calcination, the silica serves as a “skeleton” supporting the titania nanoparticles; F) The morphology and pore size can be tuned using bioengineered flagella^[28] or other biological templates such as phage and pili.

This method could be developed into a general approach for the synthesis of titania nanocomposites using other biological templates; G) Chemical modification of the templates is not required.

3. Conclusion

In summary, the present work demonstrated a new methodology to prepare double-layered titania/silica nanotubes using bacterial flagella as templates with monodispersed diameter and pore size. All reactions were carried out in aqueous solution under ambient conditions. The thickness of either layer on the nanotubes could be tuned by varying the initial concentrations of precursor solutions or the reaction time. Moreover, the morphology of the nanotubes can be easily tuned using different biotemplates. After calcination, hollow titania/silica nanotubes were obtained. The titania was transformed into a crystalline phase and condensed into nanoparticles, which were dispersed inside the supporting silica matrix. Our flagella templating approach is a facile method that is easy to scale up, environmentally friendly, and cost-efficient.

4. Experimental Section

Salmonella Flagella Purification

The frozen *Salmonella* wild type strain was inoculated in LB media (2 mL) at 37 °C with shaking (250 rpm) for overnight. Then the cell culture was inoculated in LB media (1 L) and continued to grow at 37 °C with shaking (250 rpm) until optical density (OD) reached 0.6–0.8. The culture was collected and centrifuged at 6000 g for 20 min at 4 °C. The cell pellets were washed twice by phosphate buffered saline (PBS) buffer (pH = 7.4). In the following, the cell pellet was re-suspended in deionized water by vortexing at the highest speed for 3 min. The flagella were then detached from the cells and suspended in the solution. The bacteria were removed by centrifugation at 4000 rpm for 20–30 min and the supernatant containing flagella was collected. The supernatant was centrifuged again at 10 000 g for 20 min to remove debris from solution. Flagella with high purity were precipitated by ultracentrifugation at 80 000 g for 2 h. Finally, the flagella were dissolved in either deionized water or PBS buffer.

Titania/Silica Growth on Flagella Templates

All reagents were purchased from Sigma-Aldrich without any further purification. In a typical experiment, the sol was prepared by titanium (IV) butoxide (TBT) mixed with acetylacetone (AcAc) in ethanol. They were mixed in a molar ratio of TBT:ethanol:AcAc = 1:100:5 and stirred for 1 h at room temperature. The solution was then introduced into deionized water at a volume ratio of 1:8 and stirred for 5 min. AcAc was used as a chelating reagent to slow down the hydrolysis and the condensation reactions. APTES (2×10^{-3} mmol) was added to flagella (500 μ L) solution and gently mixed by vortex. The mixed flagella solution was cooled down in an ice-water bath for 3–5 min. Then the flagella solution was added drop-wise to the sol under stirring in 3 min. The mixed solution was cooled in an ice-water bath for about 1 h and then left at room temperature for about 6 h until white precipitates appeared. The titania coated flagella nanotubes were washed with water and ethanol several times by low speed centrifugation. The synthesis of the second silica layer was based on our previous report.^[29] The procedure is similar to titania synthesis except that TEOS (2.5×10^{-2} mmol) was used as the precursor solution.

Calcinations of the Double-Layered Titania/Silica Nanotubes at Different Temperatures

Calcination of nanotubes was carried out under air in a Lindberg tube furnace (TF55030A). The air dried titania nanotubes were transferred to a porcelain boat, and heated at 110 °C for

8 h. Then, the temperature was increased (2 °C/min) to the 150 °C or 200 °C for 2 h. Finally, the samples were cooled to room temperature at a rate of 5 °C/min. Calcination of titania/silica nanotubes was performed according to the same procedure but at an increased temperature of 500 °C or 800 °C respectively for 4 h.

Materials Characterization

The titania nanotubes and titania/silica bilayer nanotubes were examined by using TEM Zeiss 10 and High Resolution TEM JEOL 2010-FX. Morphology and EDX analysis were carried out using SEM JEOL JSM-880.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

This work is supported by National Science Foundation (DMR-0847758, IIP-0930708). We also would like to thank National Institutes of Health (R01HL092526-01A2, R03AR056848-01, R21EB009909-01A1, 1R21EB015190-01A1), Oklahoma Center for Adult Stem Cell Research (434003), and Oklahoma Center for the Advancement of Science and Technology (HR06-161S and HR11-006) for financial support.

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Figure 1. SEM micrographs of flagella templated titania and double-layered titania/silica nanotubes with EDX analysis. A) Titania nanotubes; B) Titania/silica nanotubes; C) EDX analysis of titania nanotubes indicating that the nanotubes are mainly composed of titania; D) EDX analysis of double-layered titania/silica nanotubes indicating the presence of both titania and silica.

Figure 2.

TEM micrographs of titania nanotubes. A) Titania nanotubes show curved morphology characteristic of flagella; B) The rough surfaces of titania nanotubes exhibit “sticky” properties. Some redundant titania was nucleated at the interconnected sites; C) The morphology of titania nanotubes at higher magnification. The central pores can barely be observed (as marked by black arrows in C and shown in the inset).

Figure 3.

TEM micrographs of double-layered titania/silica nanotubes. A) Characteristic morphology of titania/silica nanotubes using wild type flagella as the template at low (left) and high (right) magnification; B) Tuning the thickness of titania or silica by varying the initial precursor concentration. When the concentration of titania precursor solution is reduced by half and the concentration of silica precursor solution is doubled, the flagella will be coated by less titania and more silica and the resultant titania/silica double-layered nanotubes become flatter with some free silica nanoparticles attached (A, Left Image). When the concentration of silica precursor solution is reduced by half and the concentration of titania precursor solution is doubled, the flagella will be coated with more titania and less silica. The resultant titania/silica double-layered nanotubes exhibit rougher surfaces because the first thicker layer of titania is rougher and thus the central tunnels become invisible (B, Right Image).

Figure 4.

TEM micrographs of titania nanotubes and titania/silica nanotubes with a thin layer of silica after being calcined at low temperature. A) Titania nanotubes after calcined at 150 °C for 2 h; B) Titania nanotubes after calcined at 200 °C for 2 h; C) Titania/silica nanotubes after calcined at 200 °C for 2 h, showing that after the titania nanotubes were coated with a thin layer of silica, most nanotubes stayed intact.

Figure 5. TEM micrographs of titania/silica nanotubes calcined at different high temperatures for 2 h. A) Calcined at 500 °C; B) Calcined at 800 °C (inset: high magnification).

Figure 6. HRTEM micrograph with EDX analysis of titania/silica nanotubes calcined at 500 °C for 2 h.

Figure 7. HRTEM analysis of titania/silica nanotubes to verify the phase transition. A) Detailed morphology of titania/silica nanotubes. B) High magnification image showing that dark nanoparticles are dispersed in a silica matrix and close to the central pore (tunnel). C,D) Crystal lattice fringe images showing the spacing between neighboring fringes ($D = 0.35$ nm) is corresponding to the interplanar d-spacing of (101) crystallographic planes of anatase titania phase (marked in the dash line circles).

Scheme 1.

Schematic representation of isolation of flagella and the procedure for the fabrication of double-layered titania/silica nanotubes and subsequent calcination. The calcination leads to the removal of flagella template and the transformation of titania layer from amorphous to nanocrystalline anatase phase.