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Nano Res., Just Accepted Manuscript • DOI: 10.1007/s12274-014-0571-3
http://www.thenanoresearch.com on August 26, 2014

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Just Accepted

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Templated Synthesis of TiO$_2$ Nanotube Macrostructures and Their Photocatalytic Properties

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TiO$_2$ nanotube macrostructures are directly fabricated by using carbon nanotube (CNT) sponge as templates. The porous structures show efficient photocatalytic activity with easy separation and recycle.
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ABSTRACT

Controlled synthesis of hierarchically assembled titanium dioxide (TiO$_2$) nanostructures is important for practical applications in environmental purification and solar energy conversion. We present here the fabrication of interconnected TiO$_2$ nanotubes as a macroscopic bulk material by using a porous carbon nanotube (CNT) sponge as templates. The basic idea is to uniformly coat an amorphous titania layer onto the CNT surface by the infiltration of a Ti$_2$O$_2$ precursor into the sponge and a subsequent hydrolysis process. After calcination, the CNTs are completely removed and the titania is simultaneously crystallized, which results in a porous macrostructure composed of interconnected anatase TiO$_2$ nanotubes. The TiO$_2$ nanotube macrostructures show comparable photocatalytic activities to commercial products (AEROXIDE TiO$_2$ P25) for the degradation of Rhodamine (RhB). Moreover, the TiO$_2$ nanotube macrostructures can be settled and separated from water within 12 h after photocatalysis, whereas P25 remains suspended in solution after weeks. Thus the TiO$_2$ nanotube macrostructures offer the advantage of easy catalyst separation and recycle and can be a promising candidate for wastewater treatment.

1 Introduction

TiO$_2$ is a wide band-gap semiconductor material of great interest for applications in many fields, including catalysis [1-3], solar energy conversion [4] and sensors [5, 6]. For example, TiO$_2$ nanostructures are considered as the most commonly used photocatalyst due to their high photocatalytic activity, low cost and nontoxicity [7]. In particular, TiO$_2$ nanotubes and nanotube arrays have recently attracted much interest due to their large surface area combined with high structural order. TiO$_2$ nanotubes can be prepared by sol–gel [8], hydrothermal [9-11], anodization [12], and template-assisted routes [13, 14]. Among these methods, TiO$_2$ nanotubes prepared from the sol-gel or hydrothermal methods are usually in the form of powder, which is difficult to be manipulated. Vertically aligned TiO$_2$ nanotube arrays film can be prepared by electrochemically anodizing a Ti sheet, and this organized architecture shows improved photoconversion efficiency in dye-sensitized solar cells. However, the anodization approach is limited by a waste of Ti foil with only about 2% of the foil transforming into nanotubes [15]. In addition, TiO$_2$ nanotube arrays can also be prepared by a template-assisted method. For example, porous alumina membranes (AAO) have been used as templates to fabricate vertically aligned...
TiO$_2$ nanotube arrays [16]. However, the alumina-template-assisted approach, as well as the anodization approach, is not suitable for large-scale production of TiO$_2$ nanotubes. In addition, these vertically aligned nanotubes tend to collapse into disordered powder due to low interconnectivity after the template is removed. Therefore, it remains challenging to directly synthesize well-connected TiO$_2$ nanotube macrostructures in large-scale.

Recently, we reported the growth and properties of CNT sponges [17]. These porous and flexible CNT sponges can be considered as an ideal template for the fabrication of a variety types of nanotube macrostructures, including TiO$_2$, in large-scale. CNT sponges offer four obvious advantages as templates. (1) The open-porous structure and high porosity in the sponge facilitate rapid and efficient infiltration of TiO$_2$ precursor solution into the sponge, thus CNT surface can be uniformly coated with the precursor. (2) The thickness of the TiO$_2$ layer can be well controlled by adjusting the concentration of the precursor and reaction time. Furthermore, excess precursor can be easily removed by compressing the CNT sponge due to its high elasticity. (3) The stable, three-dimensional (3D) CNT network prevents self-aggregation and ensures a homogeneous coating of TiO$_2$ on each carbon nanotube throughout the sponge. (4) The CNT sponge is in the range of centimetres, which ensures direct formation of TiO$_2$ nanotube macrostructure for easy manipulation. In this paper, we develop a simple and scalable method to fabricate TiO$_2$ nanotube macrostructures by using CNT sponges as templates. Moreover, the as-synthesized porous TiO$_2$ nanotube macrostructures have been applied for photocatalytic degradation of RhB as model of organic pollutant in water.

2 Experimental

The fabrication process of TiO$_2$ nanotube macrostructures involves three simple steps, as illustrated in Figure 1. Firstly, a hydrophobic CNT sponge prepared by chemical vapor deposition (CVD) (Figure 1(a)) was immersed in an ethanol solution containing Tetrabutyl Titanate (Ti(OBu)$_4$) precursor. The CNT sponge had a high porosity of over 99%, which allowed the TiO$_2$ precursor to rapidly and efficiently infiltrate into the open pores of the sponge. Secondly, the sponge was transferred into water, where the TiO$_2$ precursor was hydrolyzed to form an amorphous TiO$_2$ shell coating onto the CNTs surface, resulting in a black core-shell TiO$_2$-CNT sponge (Figure 1(b)). Thirdly, the TiO$_2$-CNT sponge was calcinated at 450 °C in air for 2 hours to remove the CNT templates, and a white TiO$_2$ nanotube macrostructure was obtained (Figure 1(c)). The shape of the sponge preserved during transformation from CNT to TiO$_2$-CNT, and then to TiO$_2$ nanotube macrostructure. The density of this porous TiO$_2$ nanotube macrostructure is only 0.026 g/cm$^3$, which is approximately 1/200 of the TiO$_2$ powder (4.26 g/cm$^3$), and can be supported by a piece of leaf as shown in Figure S-1 in the Electronic Supplementary Material (ESM).

3 Results and discussion

Figure 2 shows representative scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of the sponge during transformation from CNT to TiO$_2$-CNT, and then to TiO$_2$ nanotube macrostructures. The CNT sponge template is composed of entangled CNTs of 30-50 nm in diameter and up to micrometers in length (Figure 2(a), 2(b)). After the hydrolysis of absorbed Ti(OBu)$_4$ on the surface of each CNT, the CNTs are homogeneously coated with a thin TiO$_2$ layer (Figure 2(c)). The cracks marked by white arrows in the SEM image confirm the formation of core-shell TiO$_2$-CNT structures. The interface between TiO$_2$ and CNT can be identified by the contrast in the TEM image (Figure 2(d)), which gives an amorphous TiO$_2$ shell thickness of about 10 nm. The thickness of the TiO$_2$ shell can be well controlled over a wide range (5-60 nm) by changing the precursor concentration (0.06-0.24 g/mL) and hydrolysis time (10 min-2 h) (Figure S-2(a), 2(b) in the ESM). After the removal of CNTs at 450 °C, TiO$_2$ nanotubes with open tips and hollow cavities were obtained (Figure 2(e)). Compared with the core-shell TiO$_2$-CNT sponge, the diameter of the TiO$_2$ nanotubes maintained, and some short nanotubes (about 500 nm in length) appeared due to the removal of the CNTs at the cracks. TEM shows that the amorphous TiO$_2$ shells (Figure S-3(a) in the ESM) have crystallized into stucked nanoparticles (~10 nm), as shown in Figure 2(f). The lattice fringes spacing in the HRTEM of a single TiO$_2$ nanotube (Figure S-3(b)) is about 3.52 Å, corresponding to the (101) planes of anatase TiO$_2$[18].
Figure S-4 in the ESM shows the elemental mapping results of a TiO₂ nanotube of the macrostructure, which indicates the presence of carbon residue (about 3 wt%) in the TiO₂ nanotube. The carbon residue is due to both insufficient oxidization of the CNT template and also solvent residue during the TEM sample preparation process.

Figure 3(a) summarizes the powder x-ray diffraction (XRD) patterns of CNT, TiO₂-CNT and TiO₂ nanotubes. The CNT sponge template shows two distinct diffraction peaks at 26.0° and 45.0°, which can be indexed as (002) and (100) reflections of graphite [19]. For the core-shell TiO₂-CNT sponge, no diffraction peak was observed in the XRD spectra, confirming the amorphous structure of the coated TiO₂ layer. After the thermal treatment at 450 °C, the sharp diffraction peaks appeared at 25.3°, 37.8°, 48.0°, 53.9°, 55.1° and 62.8°, which can be attributed to (101), (004), (200), (105), (211) and (204) crystal planes of anatase TiO₂ [20]. These results are well consistent with the TEM characterization. The UV-Vis spectra of the CNT sponge, core-shell TiO₂-CNT sponge, and TiO₂ macrostructures (dispersed in solution) are shown in Figure 3(b). There is no absorption for CNTs between 200-800 nm. For core-shell TiO₂-CNT sponge, a broad absorption band appears at 210-275 nm, indicating a successful coating of TiO₂ shell on the surface of CNTs. After removal of CNTs at high temperature, TiO₂ nanotube macrostructures show a red-shift band range from 210-323 nm, resulting from the crystallization of the TiO₂ nanoparticles [21]. This absorption enabled the TiO₂ nanotube macrostructures as the photocatalyst to degrade dye molecules in wastewater.

To explore potential applications of the TiO₂ nanotube macrostructures for wastewater treatment, we investigated their photocatalytic activities relative to that of commercial P25. Their photocatalytic activities were evaluated by the decomposition of RhB under UV irradiation. Before illumination, the photocatalyst (5 mg of TiO₂ nanotubes or P25) was suspended in 50 ml RhB solution of 15 mg/L by slight sonication. The suspension was magnetically stirred for 1 h under dark conditions to reach the physical absorption-desorption equilibrium. Then the suspension was irradiated with UV light (200 to 400 nm) using a mercury lamp. At given time intervals during irradiation, 1 mL aliquots were sampled and centrifuged to remove the photocatalyst. UV-Vis spectra of the supernatants were characterized as shown in Figure 4(a). The absorbance of RhB dropped rapidly after irradiations, indicating effective photocatalytic degradation of the dye molecules. The concentration of RhB was determined by measuring the absorption peak at 553 nm, and normalized RhB concentrations over time during photocatalysis are summarized in Figure 4(b). The natural degradation of RhB is negligible, while the core-shell TiO₂-CNT nanotubes show obvious photocatalytic activity, where 80% of RhB was degraded within 70 min. The anatase TiO₂ nanotubes show greatly improved photocatalytic activity after calcination, and the RhB molecules were completely degraded within 70 min of irradiation. The improved photocatalytic activity is attributed to both the increased surface area by inner nanotube walls and the formation of well-defined anatase crystalline phase of TiO₂. The photocatalytic activity of anatase TiO₂ nanotubes is comparable to that of commercial P25 TiO₂ nanoparticles. However, the practical applications of TiO₂ nanoparticles for industrial applications are hampered by their removal and recycle process. Our TiO₂ nanotube macrostructures, on the other hand, can be efficiently settled and separated from water within 12 h, while P25 TiO₂ nanoparticles remain suspended in water (Figure 4(c) and 4(d)).

We further investigated the effects of calcination temperature on the phase structure and photocatalytic activity of the TiO₂ nanotube macrostructures. TiO₂-CNT core-shell nanotube macrostructures were calcinated at different temperatures from 450-650 °C, and the resulted products were named as TiO₂ NTs-450, TiO₂ NTs-550, and TiO₂ NTs-650, respectively. Figure 4(e) summarizes the powder XRD patterns of the three TiO₂ nanotube macrostructures. TiO₂-CNT core-shell nanotube macrostructures were calcinated at different temperatures from 450-650 °C, and the resulted products were named as TiO₂ NTs-450, TiO₂ NTs-550, and TiO₂ NTs-650, respectively. Figure 4(e) summarizes the powder XRD patterns of the three TiO₂ nanotube macrostructures. The diffraction pattern of the TiO₂ NTs-550 is similar to that of TiO₂ NTs-450, except for sharper peaks due to increased crystal size. Upon increasing the calcination temperature to 650 °C, some new peaks at 27.4°, 36.1° and 41.2° appeared in the XRD pattern TiO₂ NTs-650, corresponding to the (110), (101), and (111) crystal planes of the rutile TiO₂ [22], indicating some of the anatase TiO₂ have gradually transformed to the rutile phase. The photocatalytic activities of these three
TiO$_2$ nanotube macrostructures were systematically studied and the results are shown in Figure 4(f). The photocatalytic activity of TiO$_2$ NTs-550 is slightly lower than that of TiO$_2$ NTs-450, due to decreased surface area by increased domain size [23]. Furthermore, the photocatalytic efficiency of TiO$_2$ NTs-650 decreased rapidly, except for a further decreased surface area of TiO$_2$ NTs-650, the main reason is that the photocatalytic activity of rutile TiO$_2$ is much lower than that with anatase structure [24]. Thus TiO$_2$ NTs-450 is with the highest photocatalytic efficiency due to its high surface area and appropriate crystal phase structure.

4 Conclusions
We directly fabricated TiO$_2$ nanotube macrostructures by using porous CNT sponges as templates. TiO$_2$ nanotube macrostructures with different morphologies and crystalline structures were fabricated and systematically investigated for photocatalytic degradation of organic pollutants. Anatase TiO$_2$ nanotube macrostructure obtained at 450 °C shows the highest photocatalytic activity due to its high surface area and appropriate crystal phase structure. Compared with P25, the easy manipulation and separation of the TiO$_2$ nanotube macrostructures are attractive to avoid second pollution in industrial wastewater treatment.

Acknowledgements
H. Li thanks the National Science Foundation of China under the grant numbers of 51202042, Y. Fang acknowledges the National Science Foundation of China grant 21173055 for funding support.

Electronic Supplementary Material: Supplementary material (the detailed information including experimental methods, SEM images of core-shell TiO$_2$-CNT with different shell thickness, HRTEM of the core-shell TiO$_2$-CNT and TiO$_2$ nanotube macrostructures and elemental mapping of the TiO$_2$ nanotube) is available in the online version of this article at http://dx.doi.org/10.1007/s12274-***.***.

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FIGURES

(a): CNT sponge  (b): Core-shell TiO$_2$-CNT sponge  (c): TiO$_2$ nanotube macrostructure

Figure 1 The transformation from a CNT sponge to a core-shell TiO$_2$-CNT sponge and then to a TiO$_2$ nanotube macrostructure. (a) CNT sponge; (b) TiO$_2$-CNT sponge; (c) TiO$_2$ nanotube macrostructure.

Figure 2 SEM images and TEM images of the sponges in different stages. (a, b) SEM and TEM images of the CNT sponge; (c,d) SEM and TEM images of core-shell TiO$_2$-CNT sponge; (e, f) SEM and TEM images of TiO$_2$ nanotube macrostructures.

Figure 3 Comparison of the pristine CNT sponge, core-shell TiO$_2$-CNT sponge and TiO$_2$ nanotubes macrostructures in powder XRD patterns and absorption spectrum. (a) XRD patterns; (b) UV-Vis spectrum.

Figure 4 Comparison of photocatalytic efficiency of the TiO$_2$ with different structures and their separation. (a) UV-Vis of RhB solution catalyzed by TiO$_2$ nanotubes with different irradiation time; inset, RhB solutions collected at 0, 5, 10, 20, 30, 40 and 60 min; (b) Comparison of the photocatalytic efficiency of TiO$_2$ nanotubes, core-shell TiO$_2$-CNT and P25 TiO$_2$ powder; (c) The separation of TiO$_2$ nanotubes and P25 TiO$_2$ powder; (d) UV-Vis spectra of the supernatants separated from the solution catalyzed by TiO$_2$ nanotubes and P25; (e) Comparison of XRD patterns and (f) photocatalytic efficiency of TiO$_2$ NTs-450, TiO$_2$ NTs-550 and TiO$_2$ NTs-650.
Electronic Supplementary Material

**Templated synthesis of TiO\textsubscript{2} nanotube macrostructures and their photocatalytic properties**

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Supporting information to DOI 10.1007/s12274-****-****-**** (automatically inserted by the publisher)

INFORMATION ABOUT ELECTRONIC SUPPLEMENTARY MATERIAL.
1. Experimental Methods
2. Figure S-1. A 2.8cm*2cm*1cm TiO\textsubscript{2} nanotube microstructure on a piece of leaf.
3. Figure S-2. Core-shell TiO\textsubscript{2}-CNT sponge with different shell thickness
4. Figure S-3. HRTEM images of core-shell TiO\textsubscript{2}-CNT and TiO\textsubscript{2} nanotube macrostructures.
5. Figure S-4. Elemental mapping of a single TiO\textsubscript{2} nanotube.

1. Experimental Methods

**Synthesis of CNT sponges.** CNT sponges were synthesized by a chemical vapor deposition method with o-dichlorobenzene as the carbon source and ferrocene as the catalyst. Ferrocene powder was dissolved in o-dichlorobenzene to make a solution with a concentration of 0.06 g/mL. Then this solution was injected into a 2-inch quartz tube housed in a resistive furnace by a syringe pump at a feeding rate of 0.13 mL/min. The reaction temperature for the growth of CNT sponge was 860 °C. The carrier gas is Ar and H\textsubscript{2}, and their flow rates are set at a 2000 mL/min and 300 mL/min, respectively. The growth time was typically 4 h and the sponge sample was collected from the inside wall of the quartz tube after CVD.

**Synthesis of core-shell TiO\textsubscript{2}-CNT sponges.** A CNT sponge block was immersed into the ethanol solution of Ti(OBu)\textsubscript{4} with the concentration from 0.06 to 0.24 g/mL, the absorption process was proceeded on a shaker at a stirring rate of 150 rpm for 1 h. Then the Ti(OBu)\textsubscript{4} absorbed CNT sponge was transferred into a beaker filled with H\textsubscript{2}O. With an assistance of sonication for 10 min to 2 h. After stressing out the extra TiO\textsubscript{2} precursor with a piece slide glass within 2-10 s under a stress of about 10 N, core-shell TiO\textsubscript{2}-CNT sponges with shell thickness 5-60 nm were obtained. The TiO\textsubscript{2}-CNT sponge used in this paper was prepared at the Ti(OBu)\textsubscript{4} concentration of 0.12 g/mL and the sonication time is 40 min.

**Synthesis of TiO\textsubscript{2} nanotube macrostructures.** The core-shell TiO\textsubscript{2}-CNT sponge was picked up from H\textsubscript{2}O and compressed into a sheet to remove the unreacted Ti(OBu)\textsubscript{4}, then some ethanol was dipped into the sponge and the sheet like sponge recovered to its original shape. Excess Ti(OBu)\textsubscript{4} can be removed completely by repeating this process for 3 times. After a further removal of ethanol in the sponge by critical pointing drying process, the TiO\textsubscript{2}-CNT sponge was loaded in a quartz tube and heated in air at 450 °C for 2 h, and a white TiO\textsubscript{2} nanotube macrostructure was obtained.
Characterization and photocatalysis test. The morphology of CNT sponge, core-shell TiO$_2$-CNT sponge and TiO$_2$ nanotube macrostructures were characterized with SEM (Hitachi 4800) and TEM (Tecnai F20). The UV-Vis spectrum and powder XRD patterns were obtained on Perkin Elmer Lamda 950 and D/MAXTTRII with Cu Kα λ = 1.5418 Å, respectively. Photocatalytic decomposition of RhB was carried out in a beaker containing 5 mg TiO$_2$ sample and 50 mL of RhB solution (15 mg/L). UV light was produced by an Hg lamp with a filter to leave the light between 200-400 nm. Before irradiation, the RhB with TiO$_2$ catalyst was stirred in dark for 1 h to ensure the absorption-desorption equilibrium. 1 mL aliquot was taken out from the solution at given time intervals and centrifuged at 3000 rpm for 3 min (8000 rpm for 5 min for P25 TiO$_2$), then the solution was diluted by 2 mL water for UV-Vis analysis.

2. Figure S-1

![Image](image1.png)

Figure S-1 A 2.8cm*2cm*1cm TiO$_2$ nanotube microstructure on a piece of leaf.

3. Figure S-2

![Image](image2.png)

Figure S-2 Core-shell TiO$_2$-CNT sponge with different shell thickness: (a) Ti(OBu)$_4$ concentration is 0.06g/mL and sonication time is 10 min; (b) Ti(OBu)$_4$ concentration is 0.24 g/mL and sonication time is 2 h.

4. Figure S-3

![Image](image3.png)

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Figure S-3 HRTEM images of a core-shell TiO$_2$-CNT sponge (a) and TiO$_2$ nanotube macrostructure (b).

5. Figure S-4

Figure S-4 Elemental mapping of a single TiO$_2$ nanotube. The uniform distribution of C throughout the TiO$_2$ nanotube shell indicates that carbon comes mostly from the residue solvent.