# A Facile Route to Prepare Mesoporous Anatase $TiO_2$ Nanotubes Assembly

Wugang Fan[1,2] and Lian Gao*[1]
[1]*State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, P. R. China*
[2]*Graduate School of the Chinese Academy of Sciences, P. R. China*

(Received March 7, 2006; CL-060281; E-mail: liangaoc@online.sh.cn)

Anatase $TiO_2$ nanotube assembly was prepared by vapor-phase method using carbon nanotubes as template. Large surface area and mesoporous structure of the product favor the applications in gas sensing and photocatalysis.

Since the discovery of carbon nanotubes (CNTs) by Iijima in 1991,[1] intensive efforts have been devoted to fabricate various tubular nanomaterials including boron nitride (BN), boron carbide (BC) as well as ceramic oxides (e.g. $SiO_2$, $TiO_2$, and $V_2O_5$).[2] Among these, $TiO_2$ nanotubes are of considerable interest because of theirs versatile properties and potential applications such as photocatalysts, gas sensors, separator, and solar cell. Recently, Grimes and co-workers have acquired encouraging achievements on the application of $TiO_2$ nanotube arrays made by electrochemical anodization of titanium film or foil in photocleavage of water,[3] hydrogen gas sensor,[4] and dye-sensitized solar cells.[5] Up to now, there are several routes to prepare $TiO_2$ nanotubes including template method,[6] wet chemical method,[7] anodic oxidation,[8] and eletrospinning.[9] With the advance in the fields of CNTs, they have shown more and more potential in various domains, and the price is falling as a result of large scale production. Rao et al. have employed carbon nanotubes as template to prepare zirconia nanotubes successfully.[10] Recently, they used a special set-up with diaphragm pump to synthesize titania covered multiwall carbon nanotubes (MWNTs) and $TiO_2$ nanotubes; nevertheless, the pore topology and the architecture of the nanotubes were not delivered.[11] Despite the fact that fabrication of $TiO_2$ nanotubes use carbon nanotubes as template is a rational approach, there is still a short of relevant literature. Our work is aimed toward better understanding the template action of CNTs as well as fabrication of new $TiO_2$ nanostructure. We have reported previously on use of tetrabutyl titanate (TBT) as titanium source to prepare anatase $TiO_2$-coated MWNTs by vapor-phase method.[12] This method was invented by Xu et al.[13] to prepare zeolite in 1990, and the main difference from common hydrothermal synthesis is vapor transport between two separated phases during heat treatment. A detailed introduction of the methodology can be found in refs 12 and 13.

In this work, we demonstrate the preparation of $TiO_2$ nanotube assembly by vapor-phase method. It was found that the obtained nanotube assembly possessing mesoporous structure is composed of well-crystallized anatase $TiO_2$ nanoparticles and has high specific surface area.

Pristine MWNTs were prepared by decomposition of $CH_4$, with diameters ranging from 15 to 40 nm and lengths ranging from five hundred nanometers to five hundred micrometers (Shenzhen Nanotech Port Co., Ltd. China). MWNTs in a mixed concentrated acid ($H_2SO_4/HNO_3 = 3v/v$) was refluxed at 140 °C for 3 h and treated by ultrasonicating in 3-mL SDS solution (1 wt %) for 2 h. Then, this solution was rinsed with distilled water for two times and dried at 60 °C in vacuum. Dried MWNTs 20 mg was dispersed into 3-mL absolute ethanol by ultrasonication and then 0.2 mL of TBT was added dropwise into it. After the above solution being ultrasonicated for 5 min, it was transferred into a vapor-phase instrument as solid phase. Thereafter, 2 mL of distilled water was added by a pipette as the liquid phase. The sealed vapor-phase instrument was heat-treated at 100 °C for 2.5 h in an oven. Hence, the grey solid phase was washed with distilled water for three times and dried at 60 °C in vacuum. Calcination of the as-prepared sample was conducted at 550 °C for 4 h to remove MWNTs, and the sample changed from grey to white.

The obtained samples were characterized using a field-emission scanning electron microcope (FE-SEM, JEOL JSM-6700F), a transmission electron microscope (TEM, JEOL 2010) attached by an energy diffraction X-ray spectroscope (EDS, Model ISIS, Oxford Microanalysis Group), a nitrogen adsorption instrument (Micromeritics ASAP 2010), and an X-ray powder diffractometer (XRD, D/Max 2550V, Rigaku), using Cu K$\alpha$ radiation ($\lambda = 1.5418$ Å).

Following our previous study, the key point of the fabrication mechanism is that crystalline titania was firstly uniformly coated on MWNTs after hydrolysis of TBT in water vapor. After conventional calcination, $TiO_2$ nanotubes with outer diameter ca. 25–50 nm and length ranging from 0.3 to 1 μm can be formed (Figure 1). This method can reduce the hydrolysis speed of TBT by reacting in ethanol media. The $TiO_2$ nanotubes mostly are shorter than MWNTs template. We propose that after calcination some $TiO_2$ nanotubes were broken at the junctions of interweaved MWNTs. It is worthy to note that the particular assembly of $TiO_2$ nanotubes has a great number of tube-to-tube contact points and should possess high conductivity. This character combining with large surface area can bring great enhancement of gas sensitivity.[4]

The architecture of individual $TiO_2$ nanotube is investigated by TEM (Figure 2). It was found that the nanotube is consisted

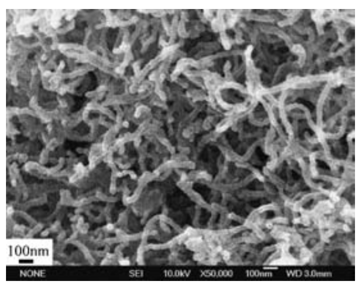


**Figure 1.** FE-SEM image the $TiO_2$ nanotubes assembly.

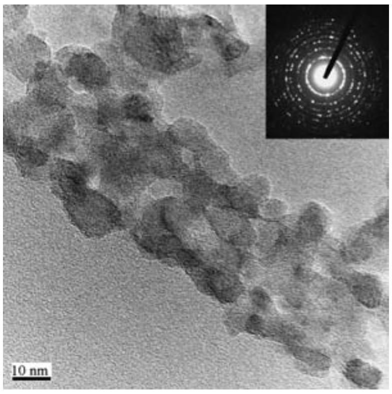


**Figure 2.** TEM image the anatase $TiO_2$ nanotube.

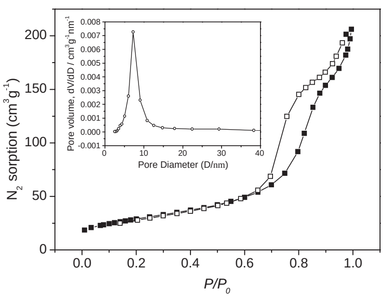


**Figure 3.** Nitrogen adsorption–desorption isotherm and pore size distribution (inset) for the $TiO_2$ nanotube assembly.

of $TiO_2$ nanocrystals with different crystal plane, e.g., (101), (200). The nanoparticles with good crystallinity[12] and increased size (<10 nm) after calcination stack up the long tube-like structure by directing action of MWNTs. Selected area electron diffraction (SAED) also shows that the nanotubes are multi-crystalline in nature and correspond to anatase structure.

The nitrogen adsorption isotherm of the $TiO_2$ assembly was examimed to study the pore structure of $TiO_2$ nanotubes (Figure 3). The absorption isotherm exhibits a type IV, suggesting the presence of mesopores. The type of hysteresis loop of $N_2$ isotherm is intermediate between H1 (at $0.6 < P/P_0 < 0.8$) and H3 (at $P/P_0 > 0.8$). The feature of the hysteresis loop correlates to typology to some extent. Usually, H1-like hysteresis loop is indicative of uniform mesopores with cylindrical geometry. The hysteresis extended to $P/P_0 = 1$, suggesting that the presence of large pores which are not being filled. The large pores correspond to the pores between the nanotubes. The BET surface area and pore volume of the sample were measured to be 139.8 $m^2\,g^{-1}$ and 0.3 $cm^3\,g^{-1}$, respectively. The pore volume distribution curve for $TiO_2$ nanotubes is obtained form the desorption data using BJH algorithm (Figure 3 inset). It can be found that the pore size distribution is sharp and the average pore diameter is estimated to be 9.1 nm. This hierarchical structure of $TiO_2$ nanoparticals with mesopores structure also provides extremely benefit for catalytic applications.[14]

Figure 4 shows the XRD pattern of $TiO_2$ nanotube assembly. The peak position agrees well with the reflection of $TiO_2$ (anatase phase). The crystallinity is high and the width of the

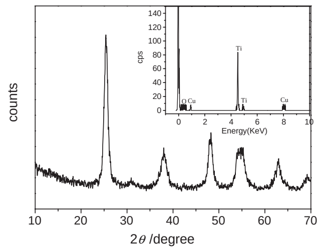


**Figure 4.** XRD pattern and EDS of the $TiO_2$ nanotubes.

reflections is broadened. The average crystal size estimated by the Scherrer equation is up to 9.4 nm. In contrast to titania nantubes prepared from $TiO_2$ power by wet chemical method,[15] this approach tends to obtain a product with pure phase $TiO_2$. Elemental analysis using EDS indicates the presence of Ti and O in the $TiO_2$ nanotubes.

In summary, we developed a simple and efficient route to prepare well-organized $TiO_2$ nanotube assembly with MWNTs as a template. The length of the resulting nanotubes reaches micrometer and a large number tube-to-tube contact points exist. The $N_2$ aborption–desorption data shows that the materials have uniform pseudo-cylindrical mesoporous and large surface area. These characters favor the applications as a gas sensor and photocatalysts.

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