

Synthesis and characterization of one-dimensional titanate nanostructures via an alkaline hydrothermal method of a low surface area TiO₂-Anatase

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In this paper, both nanotubes and nanowires were synthesized directly using a cheap precursor (low surface area TiO₂) via a simple hydrothermal process without using any sacrificial templates. The synthesized materials were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and accelerated surface area and porosimetry apparatus (ASAP). Transmission electron microscope observations showed that nanotubes were formed with an inner diameter of 2–3.5 nm, an outer diameter of 8–10 nm, and an open-ended shape. The nanotubes showed IV-type isotherms with H₃ type hysteresis loop according to BDDT (Brunauer, Deming, Deming, and Teller) classification, indicating the presence of mesopores. Significant increases of specific surface area (277.82 m²/g) and pore volume (1.08 cm³/g) have potential applications such as in catalysts, sensors, high efficient solar cells, for hydrogen storage, as absorbents, etc. With an increase in the hydrothermal temperature, the morphology transformed to nanowires and the surface area and pore volume decreased.

Key words: Nanostructure, Hydrothermal, Nanotube, Titanate, Nanowire.

Introduction

Dimensionality is a crucial factor in determining the properties of nanomaterials [1] and, thus, the control of size and shape is of great interest. In contrast to size control, shape control of particulates is a more difficult and challenging topic. One dimensional (1D) nanostructured materials such as nanotubes and nanowires have become one of the hottest research fields. The anisotropic morphology of one dimensional nanostructures gives superior optical, magnetical, electrical, and mechanical properties [2, 3]. Since carbon nanotubes were reported by Iijima [4], nanotubular materials have attracted great attention because of their intrinsic multi functionality that arises from four different contact regions such as tube opening, outer surface, inner surface, and interstitial region [5]. Their unique properties impart on them potential applications in catalysis, hydrogen storage devices, highly effective solar cells, gas sensors, microelectronic devices, and microscope probe tips [5–7].

Currently, there have been developed different methods of synthesis of one dimensional nanostructured materials. Depending on the synthesis method, the size of one dimensional nanostructured materials can vary from sub-nanometre to tens of nanometres. Various templates, such as porous alumina membranes, and organogelators have been used to prepare nanotubes and nanowires.

However, the templating method is not appropriate for preparing smaller nanotubes and nanowires due to the limitation of the size of template. The templating method is an elaborate and time-consuming process. Among synthesis approaches, the hydrothermal route is a powerful and promising strategy for preparing 1-D nanomaterials. Hydrothermal treatments are an easy route to obtain nanotubes and nanowires, owing to their being cost-effective without using any surfactant or template, feasibility, and availability of widespread applications [8, 9].

Titanates are well-known as functional ceramic materials (dielectric, piezoelectric, ferroelectric, and low absorption of infrared radiation) and titanate fibers (whiskers) are widely used as structural reinforcements in polymers, metals, and ceramic composites [10–12]. Moreover, titanium dioxide (TiO₂) is one of the most important metal-oxides. These oxides have recently found advanced applications [13]. There is also great interest in the development of titanates and TiO₂-based solids with nanoscale dimensions and high morphological specificity. These synthesized nanostructured materials may be significant in understanding dimensionally-confined transport phenomena and developing new materials. Ion-exchange and intercalation of other metal ions and organic molecules may lead to functionalization of titanate nanostructures for future applications [10–12].

In this study, the synthesis of one-dimensional titanate nanostructures via an alkaline hydrothermal method of low surface area TiO₂ was investigated. The synthesized products have been characterized as nanotubes and nanowires depending on the applied hydrothermal temperature.

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Experimental Procedure

Materials and instruments

The initial TiO_2 powder was supplied by the Riedle-de Haën company from Germany (it is called RH) which has a purity of $>99.5\%$ and a low BET surface area (Brunauer-Emmet-Teller method) of $10 \text{ m}^2/\text{g}$. RH has a 100% anatase crystal structure. Fig. 1 shows a TEM image of raw material. The size of particles is 150 nm. Sodium hydroxide (10 N) and HCl (37%) was obtained from Aldrich and Merck, respectively without further purification. Deionized water was used throughout the whole experiment.

XRD patterns were recorded using a Philips PW1840 diffractometer, with $\text{Cu-K}\alpha$ radiation $\lambda = 0.154 \text{ nm}$ and a graphite monochromator in the 2θ range of 10° – 80° . The external features and morphology of the synthesized materials were analyzed using a high-resolution transmission electron microscope (HR-TEM, Philips CM 200 FEG) and scanning electron microscope (SEM, Cambridge Instruments). The pore structure of the TiO_2 -derived nanomaterials was characterized by N_2 adsorption at -196°C using an adsorption apparatus (Micrometrics, ASAP2010). BET surface area was calculated from the linear part of the BET plot ($P/P_0 = 0.05 - 0.3$). Total pore volume was taken from the volume of N_2 adsorbed at $P/P_0 = 0.995$. The average pore diameter was estimated using the adsorption branch of the isotherm and the Barrett-Joyner-Halenda (BJH) formula.

Method

TiO_2 powder was dispersed in an aqueous solution of NaOH (10 N) under vigorous magnetic stirring for about 1 h to form a white suspension, followed by placed it into a Teflon-lined autoclave at different temperatures (110°C and 160°C) and for a given time. After hydrothermal processing, the mixture was allowed to cool to room temperature. The precipitate was repeatedly centrifuged and rinsed with distilled water and then with HCl solution until $\sim\text{pH} = 6-7$. The powders were dried in air at 100°C for 24 h to give the as-synthesized product. Then the products were calcined at 300°C .

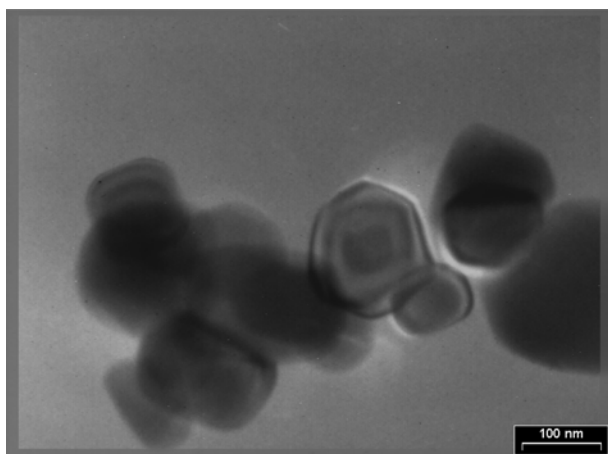


Fig. 1. TEM image of raw material.

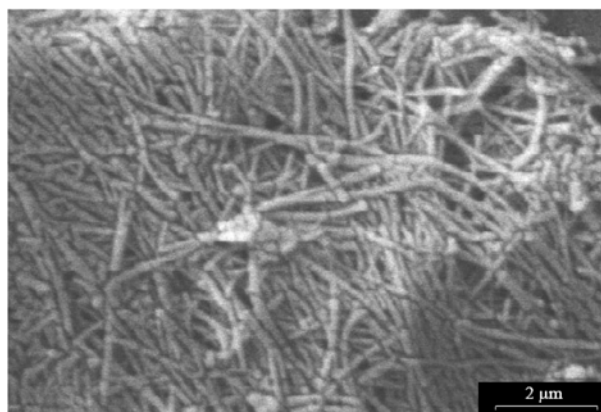


Fig. 2. SEM image of sample synthesized at 110°C .

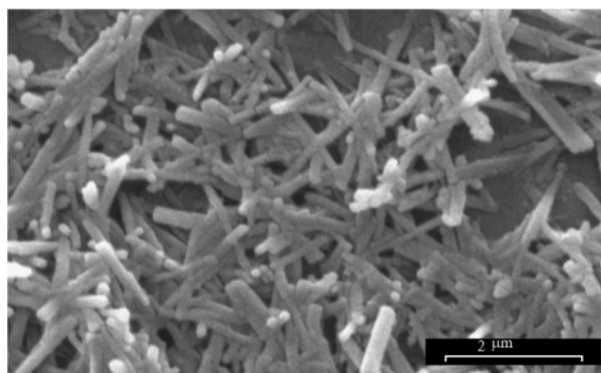


Fig. 3. SEM image of sample synthesized at 160°C .

Results and Discussion

SEM images of the samples revealed that in both cases the starting spherical titania particles were fully transformed. The SEM image of the sample as-synthesized at 110°C in Fig. 2 shows numerous fibrous structures that lie close to each other. They tend to stick to each other, forming a raft-like material. In Fig. 3, the SEM image of the sample synthesized at 160°C shows that this is composed of rod-like structures with a larger diameter, but mostly without any order in their orientation. The TEM image (Fig. 4) shows that these short rods are in fact, nanowires with diameters less than 40 nm.

Fig. 5 shows TEM images of the sample as-synthesized at 110°C from RH as the raw material. The TEM images show that the products were fine hollow open-ended tubes with a uniform diameter along their lengths. The tubes have an outer diameter ranging from 8–10 nm and an inner diameter of 2–3 nm. The low resolution TEM image of the as-synthesized sample at 160°C (Fig. 4) indicates the presence of large proportions of nanowires with a typical diameter of 20–40 nm and a length of 2–10 μm. The increasing hydrothermal temperature was found to facilitate the formation of nanowires. Despite containing some nanotubes, the obtained sample at the higher temperature actually is composed of abundant nanowires. A few nanotubes were observed attached to the surface of the nanowires.

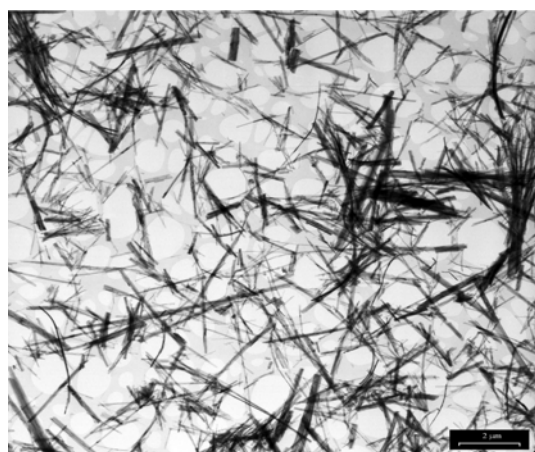
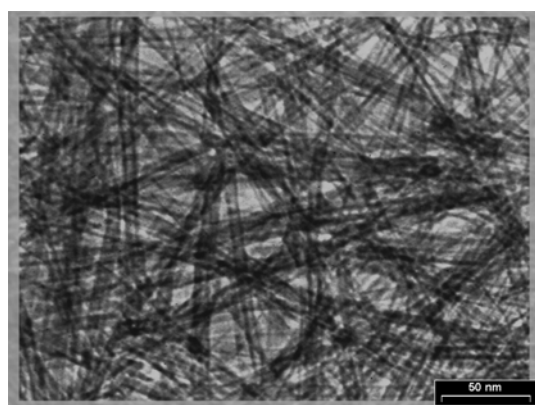
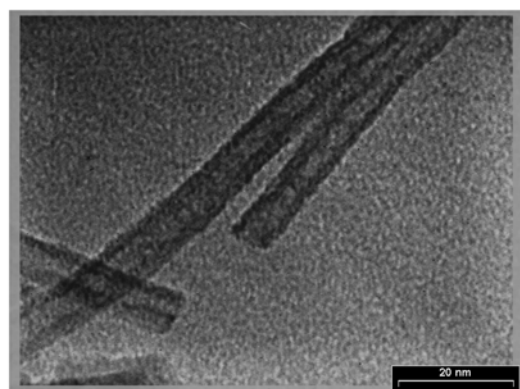


Fig. 4. TEM image of nanowires.



(a)



(b)

Fig. 5. TEM images of nanotubes: (a) low magnification (b) high magnification.

Fig. 6 shows the XRD patterns of the synthesized nanotubes and nanowires. Low peak intensities and substantial peak widths show the poor crystallinity and nanosize of the structures. There are very much different from the diffraction pattern of TiO_2 . The characteristic peak at around $2\theta < 10^\circ$ indicates that the structures of nanotubes and nanowires both appear to be layered titanates. These patterns are similar to layered titanate structures such as $\text{H}_2\text{Ti}_3\text{O}_7$ and $\text{H}_x\text{Ti}_{2-x/4}\square_{x/4}\text{O}_4$ ($x = 0.75$). As shown in Fig. 6, when the hydrothermal temperature was increased,

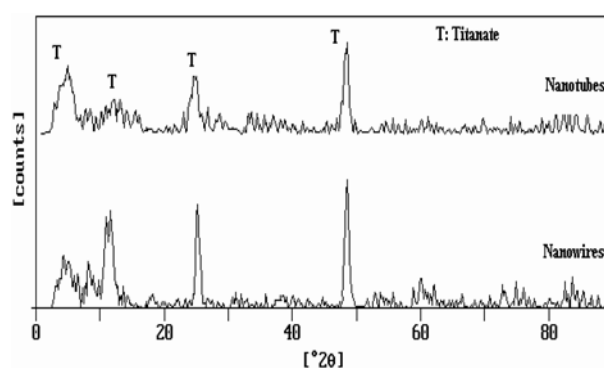


Fig. 6. XRD patterns of synthesized nanotubes and nanowires

the intensity of peaks increased, but the peak intensity at around $2\theta < 10^\circ$ decreased due to a decrease in the interlayer spacing.

In samples synthesized from RH, the amounts of specific surface areas and pore volumes are high in comparison with the starting material. When RH was transformed into the titanate nanotubes, there was a significant increase in the specific surface area from $10 \text{ m}^2/\text{g}$ to $277.82 \text{ m}^2/\text{g}$ (by a factor about 28 times) and for the pore volume up to $1.08 \text{ cm}^3/\text{g}$ due to the transformation to nanotube structures. Figs. 7 and 8 show the nitrogen adsorption-desorption isotherm and pore size distribution measured on the samples examined. The nanotubes showed a IV-type isotherm with a H_3 type hysteresis loop according to the BDDT classification, indicating the presence of mesopores. Considering the morphology of the nanotubes observed in Fig. 5b and Fig 8, the smaller pores ($< 10 \text{ nm}$) may correspond to the pores inside the nanotubes and the diameters of these pores are equal to the inner diameter of the nanotubes, while the larger pores ($10\text{--}100 \text{ nm}$) can be attributed to the aggregation of the nanotubes.

Interestingly, a change in the synthesis conditions may lead to marked differences in the structural properties. The nanotubes have a specific surface area of $277 \text{ m}^2/\text{g}$, and a pore volume $1.08 \text{ cm}^3/\text{g}$ whereas the surface areas and pore volume of nanowires are $88.63 \text{ m}^2/\text{g}$ and $0.27 \text{ cm}^3/\text{g}$, respectively. The main difference between nanotubes and nanowires thus seems to be in their surface morphology. In the nanowire morphology according to Fig. 7, the hysteresis loop shifts to the region of higher relative pressure and the area of the hysteresis loop gradually becomes small. Further observation from Fig. 8 indicates that the average pore size of the samples increased from 67 to 104 nm due to the tube structure collapsing with a change in the morphology from a nanotube to a nanowire.

Conclusions

The main conclusions derived from this study are as follows:

1. High purity nanotubes and nanowires could be controllably obtained by the hydrothermal treatment of

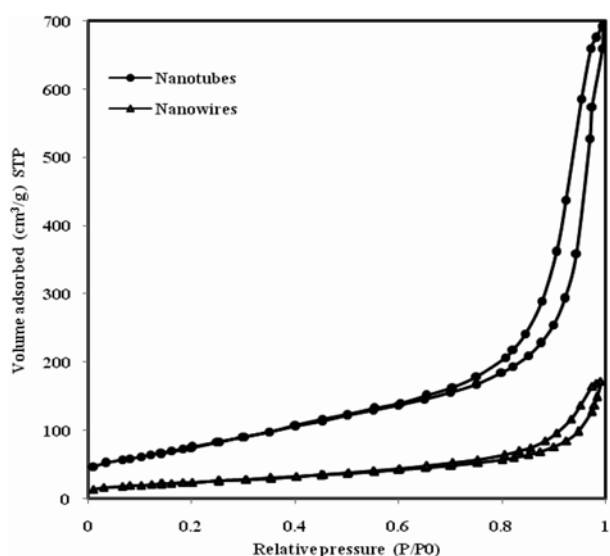


Fig. 7. Nitrogen adsorption-desorption isotherm measured on nanotubes and nanowires.

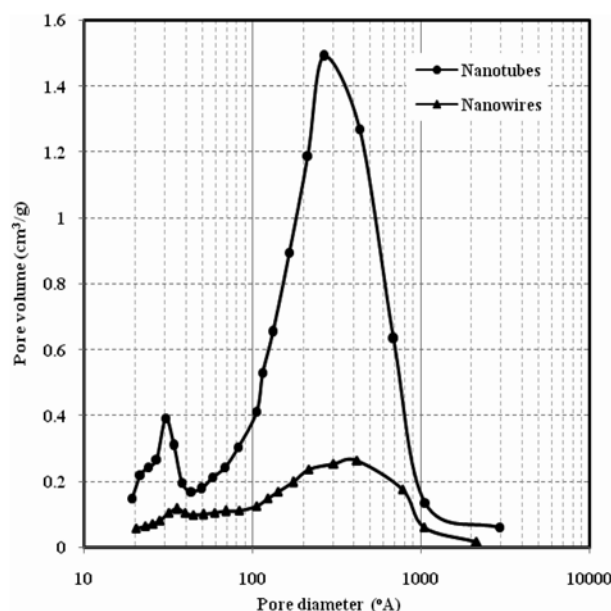


Fig. 8. Pore size distribution measured on nanotubes and nanowires.

anatase TiO_2 in concentrated NaOH solution depending on the treatment temperature. This indicates that the temperature parameter plays a determining role regarding the product morphology.

2. The crystalline structure of nanotubes and nanowires are similar to layered titanate structures such as $\text{H}_2\text{Ti}_3\text{O}_7$ and $\text{H}_x\text{Ti}_{2-x/4}\square_{x/4}\text{O}_4$ ($x=0.75$).

3. The synthesized titanate nanotubes have a multiwall, an outer diameter ranging from 8-10 nm and inter diameter of 2-3 nm.

4. The nanotubes showed a IV-type isotherm with a H_3 type hysteresis loop according to BDDT classification, indicating the presence of mesopores.

5. Significant increases for the specific surface area ($277.82 \text{ m}^2/\text{g}$) and pore volume ($1.08 \text{ cm}^3/\text{g}$) have potential applications such as in catalysts, sensors, energy generation, medical, etc.

6. Increasing the hydrothermal temperature was found to facilitate the formation of nanowires with a typical diameter of 20-40 nm and a length of 2-10 μm .

7. The structural change from a nanotube to a nanowire shape resulted in a rapid decrease in the surface area and pore volume and an increase in the peak pore size due to annihilation of the inner pore of the nanotubes.

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