Available online at www.sciencedirect.com

SCIENCE DIRECT

Materials Letters 59 (2005) 1142–1145

materials letters

www.elsevier.com/locate/matlet

Synthesis of bundle-like structure of titania nanotubes

Hongrui Peng[a,b], Guicun Li[a,b], Zhikun Zhang[b,*]

[a]Fishery College, Ocean University of China, Qingdao 266002, P.R. China
[b]Key Laboratory of Nanostructured Materials, Qingdao University of Science and Technology, Qingdao 266042, P.R. China

Received 24 May 2004; received in revised form 24 November 2004; accepted 2 December 2004
Available online 24 December 2004

Abstract

Bundle-like structure of titania nanotubes has been synthesized via the reaction of anatase titania nanoparticles and NaOH aqueous solution at higher treatment temperatures (higher than 190 °C) after calcination at 500 °C for 1 h. The bundle-like structure of titania nanotubes is characterized by transmission electron microscope (TEM) and field-emission scanning electron microscope (FE-SEM). The tubular structures of titania with diameters of 5–15 nm are confirmed by TEM. The effects of treatment temperatures on the morphologies of titania nanostructures are investigated. As SEM images show, when the treatment temperature is 170 °C, randomly oriented structure of titania nanotubes coexisting with titania nanobelts are obtained. However, bundle-like structure of titania nanotubes with lengths of several micrometers are fabricated at high treatment temperatures (higher than 190 °C). X-ray diffraction (XRD) pattern shows that anatase phase titania nanotubes are synthesized after calcination at 500 °C for 1 h.

Keywords: Bundle-like structure; Nanotube; Nanobelt; Chemical process; Titania

1. Introduction

Since the discovery of carbon nanotubes [1], one-dimensional (1D) nanostructured materials have attracted intensive interest because of their novel physical properties and potential applications. Titania is an n-type semiconductor and widely used as photocatalysts [2,3], carrier of catalysts [4], photovoltaic cell [5,6], photoelectrode [7] and photonic crystal [8]. Recently, various templates, such as porous alumina [9–11], organic eggshell membrane [12] and surfactant assemblies [13–15] were used to prepare titania nanofibers or nanotubes. These nanotubes generally have large diameters, and their walls are composed of nanoparticles. Chemical processing method was also developed to synthesize titania nanotubes. This process is more convenient than template methods in which special templates are always removed by solution etching or calcination. In these cases, anatase or anatase-rutile titania nanoparticles were treated with an aqueous solution of 10 M NaOH at lower than 150 °C to fabricate titania nanotubes. The formation mechanism of titania nanotubes was in controversy [16–21]. Kasuga et al. [17] believed that titania nanotubes were formed after washing with distilled water and HCl aqueous solution. Du et al. [19] reported that titania nanotubes were obtained before the washing treatment. However, the synthesis of bundle-like nanostructure of titania has rarely been reported. Yuan et al. [22] used amorphous titania gel as precursor to synthesize hierarchical interlinked structure of titania nanofibers. In this letter, we report the synthesis of bundle-like structure of titania nanotubes by chemical process at high treatment temperature (higher than 190 °C).

2. Experimental

2.1. Materials

Titanium tetrabutoxide (Xinhua Institute of Active Materials, Changzhou, China), butyl alcohol (Hengda Chemical

* Corresponding author. Tel.: +86 5324022869; fax: +86 5324022869.
E-mail address: zhangzk@public.qd.sd.cn (Z. Zhang).

0167-577X/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.matlet.2004.12.001

Plant, Shanghai, China) and NaOH (Jiangshan Chemical Plant, Qingdao, China) were all analytical grade and were used without further purification. Deionized water was used in the experiments.

2.2. Preparation of bundle-like structure of titania nanotubes

Anatase TiO_2 particles with diameters of 20–30 nm used in the study were prepared by the hydrolysis of titanium tetrabutoxide in butyl alcohol solution and calcination at 500 °C for 1 h. The bundle-like structure of titania nanotubes was synthesized at high temperature by using a similar process to that reported by Kasuga et al. [16,17] 1 g of anatase TiO_2 particles was mixed with 50 mL of 10 M NaOH aqueous solution in a Teflon vessel. The mixture was then placed in a stainless steel vessel and maintained at 210 °C for 24 h. The precipitate after hydrothermal treatment was separated by centrifugation and washed with deionized water until the pH value of the supernatant was about 7. The product was further dried under vacuum for 10 h and calcined at 500 °C for 1 h.

2.3. Characterization

Bundle-like structure of titania nanotubes was characterized by TEM and FE-SEM. TEM images and electron diffraction pattern were obtained on a JEM-2000EX microscope, using an accelerating voltage of 160.0 kV. TEM samples were prepared by dispersing the powder in alcohol by ultrasonic treatment, dropping onto a copper grid coated with carbon support film. SEM measurements were conducted on a JSM-6700F field-emission scanning electron microscope. Before SEM imaging, the samples were sputtered with thin layers of gold. XRD analysis was performed on a D/max-2500 X-ray diffractometer.

3. Results and discussion

Fig. 1 shows that TEM images of the as-prepared titania nanotubes synthesized at 210 °C and then calcined at 500 °C for 1 h. Nanoscale fibrillar structures washed with deionized water are found in a low magnification TEM image (Fig. 1A). The lengths of titania fibers are about several hundred nanometers. The titania fibrillar structures usually align together. The TEM image at a higher magnification (Fig. 1B) reveals that titania fibers contain open-ended tubular structures, indicating that the formation of titania nanotubes has not much to do with the acid treatment in agreement with the finding of Du et al. [19]. The diameters of titania nanotubes are in the range of 5–15 nm. The titania nanotube can be fractured as indicated by an arrow possibly due to ultrasonic vibration.

The effects of treatment temperatures on the morphologies of titania nanotubes were investigated. It is found that the morphologies of titania were not changed before and after calcination at 500 °C [17]. Fig. 2 shows SEM images of nanoscale fibrillar titania structures with different treatment temperatures and then calcined at 500 °C for 1 h. As shown in Fig. 2A, bundle-like titania fibrillar structures are synthesized at 210 °C (Fig. 2C). It is clear that these titania nanotubes self-assemble into bundle-like superstructures. The lengths of the nanoscale fibrillar titania structures were about several micrometers and the diameters are in the range of 30–40 nm. In comparison with Fig. 1, it is indicated that the nanoscale fibrillar

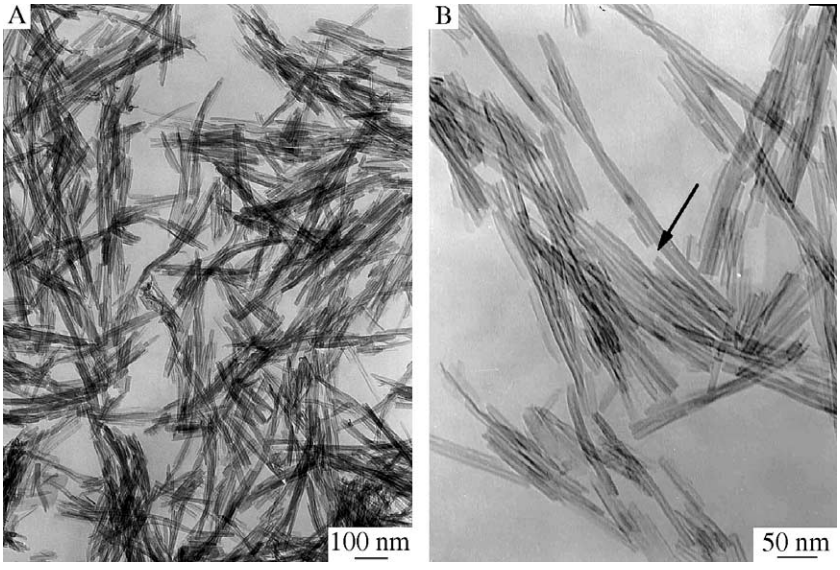

Fig. 1. TEM images of titania nanotubes synthesized at 210 °C and then calcined at 500 °C for 1 h. (A) low magnification, (B) high magnification.