Hindawi Publishing Corporation
Journal of Nanomaterials
Volume 2013, Article ID 610964, 6 pages
http://dx.doi.org/10.1155/2013/610964

Research Article

Facile Synthesis of Template-Induced SnO_2 Nanotubes

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Received 28 April 2013; Accepted 28 May 2013

Academic Editor: Yanqiu Zhu

Large scale SnO_2 nanotubes are successfully obtained by a facile hydrothermal method at a mild temperature. The morphologies and the microstructures of the as-synthesized SnO_2 products are characterized by scanning electron microscope (SEM) and transmission electron microscope (TEM). The average diameter of the nanotubes is about 100 nm. The phase and composition of the as-obtained products are investigated by X-ray diffraction (XRD). A series of comparison experiments were conducted by varying the experimental parameters, such as temperature, time, and the amount of the alkali, to study the formation mechanism of SnO_2 nanotubes.

1. Introduction

Due to their unique structures and novel performances different from the corresponding bulk counterparts, one-dimensional or quasi-one-dimensional nanomaterials are attracting more and more attention. So far, a variety of one-dimensional nanostructures have been synthesized, such as nanospirals [1, 2], nanowires [3–7], nanotubes [8, 9], and nanobelts [10–12]. Therein, the tubular structures show good prospects for the applications in the field of sensors, catalysis, and photovoltaic conversion because of their excellent physical and chemical properties [13, 14]. Since Iijima found the carbon nanotubes in 1991 [15], people's interests in tubular structure have been thriving. Thus far, different tubular structures have been synthesized by many methods, such as TiO_2 [16], SnO_2 [17], ZnS [18, 19], $NaNbO_3$ [20], and V_2O_5 [21].

SnO_2 is a very important functional metal oxide material with the direct band gap of 3.6 eV at room temperature. Owing to the large specific surface area and aspect ratio, one-dimensional SnO_2 nanostructures have wide applications in optical, electronic, and photocatalytic fields [22–25]. Among them, tubular structure is especially interesting due to their hollow characteristics. Jia et al. reported a kind of hydrothermal method to synthesize the SnO_2 nanotubes [26]; Salehi synthesized SnO_2 nanotubes using the vapor thermal evaporation method at 900°C [27]; Kim and coworkers prepared SnO_2 nanotubes through a penetration method [28]; Lai et al. synthesized SnO_2 nanotubes through a size-controlled electrochemical way at room temperature [29]; Wang et al. prepared SnO_2 nanotubes by the molten salt assisted, deposited SnO_2 on the a-MoO_3 nanorods [30]. Herein, we reported a simple template-induced hydrothermal method to synthesize high yield SnO_2 nanotubes. The growth mechanism of the as-synthesized SnO_2 nanotubes was also proposed.

2. Experimental Details

2.1. Purification of Carbon Nanotubes. All reagents were of an analytical grade and used without further purification. In a typical synthesis procedure, 1 g of MWCNTs was dispersed into 30 mL of thick HNO_3 and heated to boiling reflux for 12 h. After the acidification treatment, the MWCNTs were washed several times with deionized water to neutral. Finally, the product was dried in a chamber at 130°C for 12 h and treated at nitrogen atmosphere at 600°C for 3 h.

2.2. The Preparation of SnO_2 Nanotubes. 1.0500 g of $SnCl_4{\cdot}5H_2O$ was added to 0.57 mol/L of sodium hydroxide solution (35 mL) under stirring unceasingly at room temperature. And then 0.0500 g of treated carbon nanotubes was added into the above solution. After stirring for 20 min, the solution was transferred into a PTFE-line autoclave with a volume of 50 mL. The autoclave was sealed and kept at 160°C

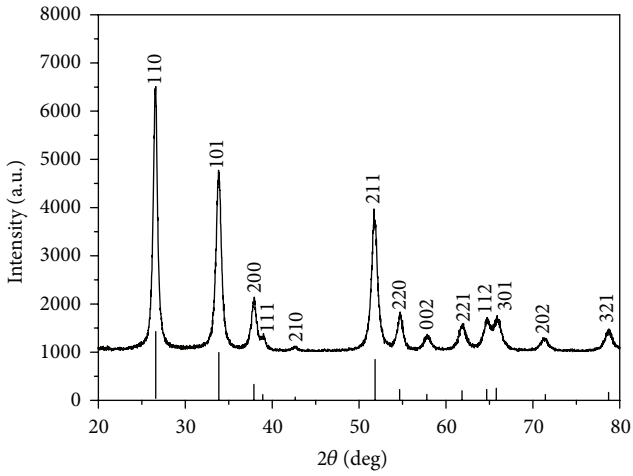


Figure 1: XRD pattern of the as-synthesized SnO_2 nanotubes.

for 14 h. Then the mixture solution was washed several times with ethanol and deionized water, respectively. Finally, the solid black product was dried in a chamber furnace at 80°C for 10 h and annealed in a muffle kiln at 600°C for 2 h.

The phase and composition of the as-obtained product were characterized by X-ray diffraction (XRD, Rigaku Dmax-rB, Cu Kα radiation, $\lambda = 0.1542$ nm 40 KV, 100 mA). The morphology and microstructure of the samples were studied by scanning electron microscope (SEM, Hitachi-4800) and transmission electron microscope (TEM, JEOL 2010EX).

3. Results and Discussion

The XRD pattern shown in Figure 1 showed that all the diffraction peaks can be indexed to the rutile tetragonal SnO_2 in accordance with the standard PDF card (number 41-1445). No obvious diffraction peaks from other impurities were detected, indicating high purity of the as-synthesized product. Carbon diffraction peaks were not found, revealing oxidation and decomposition of carbon nanotubes during calcination.

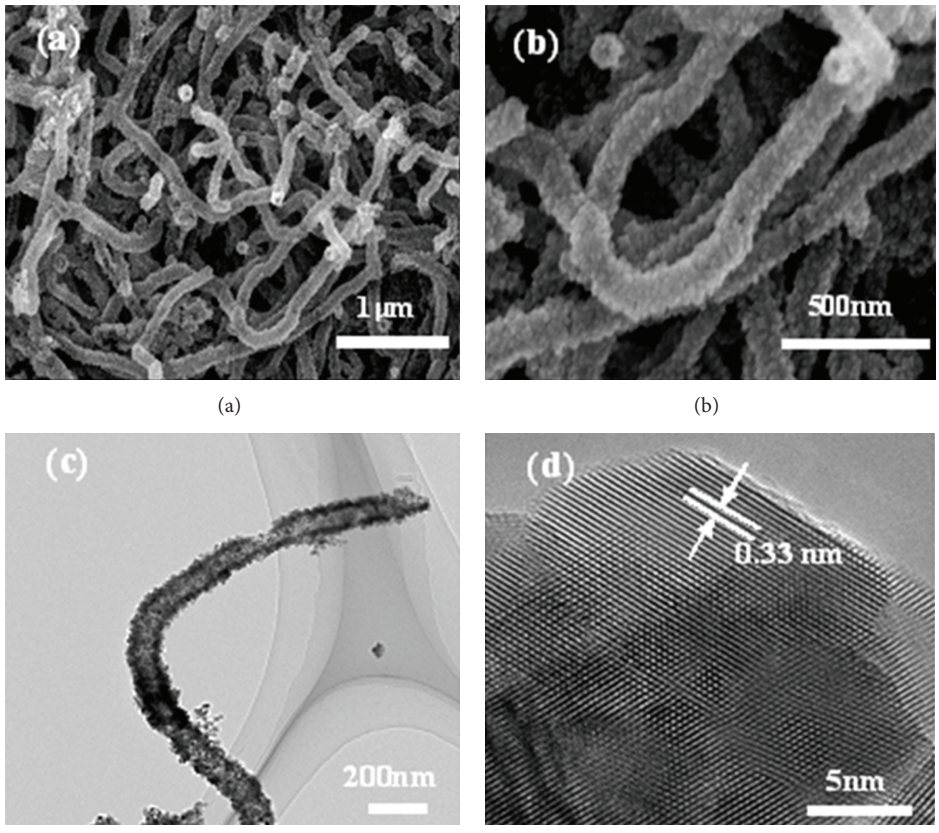
Morphology characterization was conducted using SEM and TEM. A typical low magnification SEM image was shown in Figure 2(a), finding large quantities of wire-like structures that were formed. Figure 2(b) shows high magnification SEM image, where there are some particles dispersed on the surface of the wire-like structure. The length of the wire-like structure is several micrometers, and the average diameter is about 50 nm. TEM was used to further characterize the morphology and microstructure of the product. Typical low magnification TEM image of the as-synthesized single SnO_2 structure was shown in Figure 2(c). One finds that the wire-like structure is hollow, named as nanotube. HRTEM image in Figure 2(d) indicated that the as-prepared products are highly crystalline. The measured lattice distance is 0.33 nm, corresponding to the rutile SnO_2 (110) plane.

In order to study the formation mechanism of SnO_2 nanotubes, a series of comparison experiments were conducted by varying the experimental parameters. First, we discuss the effect of the amount of alkali on the morphology of the as-synthesized product. Figure 3 showed SEM images of the as-synthesized products at 160°C for 14 h with different NaOH concentrations. When the concentration of NaOH was 0.29 mol/L, small irregular SnO_2 nanoparticles could be found, as shown in Figure 3(a). Increasing NaOH amount to 0.57 mol/L, many uniform nanotubes with rough surface could be observed (Figure 3(b)); the outer diameter of the nanotubes is about 100 nm, and inner diameter is about 50 nm. Then when increasing NaOH concentration to 0.86 mol/L, still some nanotubes were formed, but the surface of the product becomes smooth (Figure 3(c)). When the amount of NaOH is reaching 1.1 mol/L, no nanotubes appeared. This shows that the amount of alkali played a key role in the formation of the SnO_2 nanotubes.

Temperature-dependent experiments were also conducted. With the other growth parameters kept constant, when reaction temperatures are 90°C and 160°C, respectively, the diameter of nanotubes is about 100 nm and the thickness is about 50 nm, but the wall of the nanotube is thinner at low temperature (shown in Figures 4(a) and 4(b)). Further increasing the temperature to 200°C, the products are nanospheres with rough surface whose diameter is about 100 nm (Figure 4(c)). Not any product appeared when annealing at room temperature.

Finally, we discuss the effect of reaction time on the morphology of the as-synthesized products. When reaction time reaches 6 h, some irregular nanoparticles appear, as shown in Figure 5(a). With the reaction time elevated to 10 h, 14 h, and 18 h, the morphology of the products is SnO_2 nanotubes, and the diameter of the nanotubes is about 200 nm (Figures 5(b)–5(d)). This revealed that the reaction time has a certain effect on the morphology of the products. The formation of nanoparticles might be due to short reaction time, and there is not enough time for the nanoparticles to be adsorbed to carbon nanotubes. After annealed at 600°C, carbon nanotubes are removed, only some SnO_2 nanoparticles are left. When increasing the reaction time to 10 h, the SnO_2 nanoparticles adsorbed on carbon nanotubes are relatively less, and when the reaction time becomes longer, more SnO_2 nanoparticles are adsorbed to the outer wall of carbon nanotubes, and SnO_2 nanotubes were formed after carbon nanotubes were calcined.

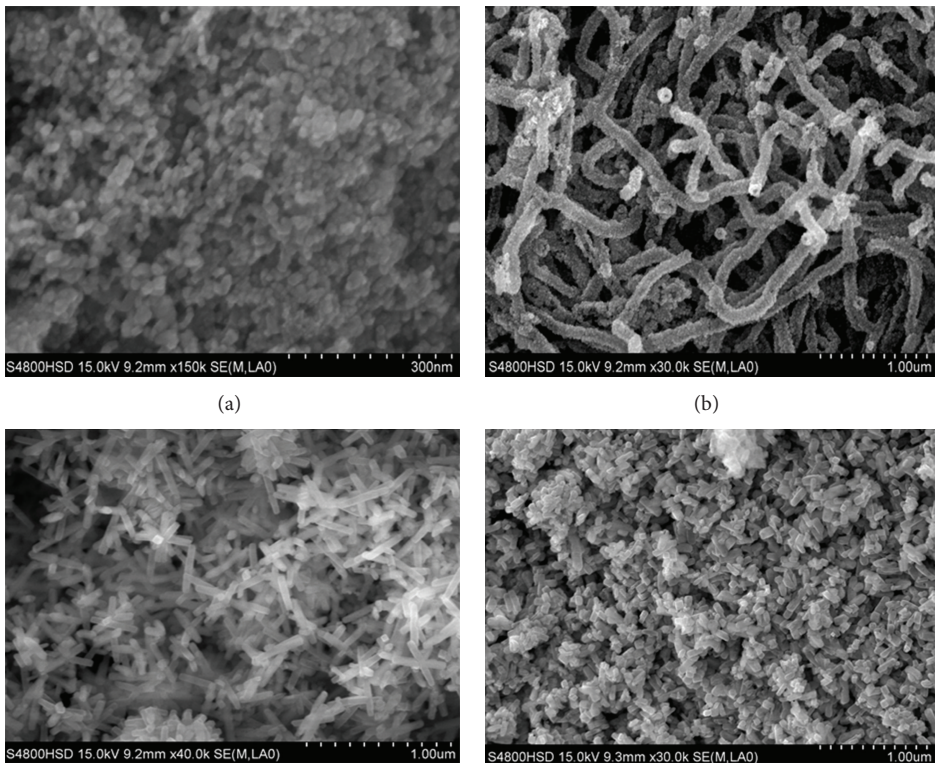
Based on the above mentioned results, a possible growth mechanism of SnO_2 nanotubes can be initially proposed as follows. First, Sn^{4+} reacts with OH^- and forms $Sn(OH)_4^+$ particles in alkali solution as a nucleus, and the formed small particles are further converted to SnO_2 particles. Meanwhile, SnO_2 crystal nucleus is immediately gathered in the outer surface of the carbon nanotubes. When annealed in the air at 600°C, internal carbon nanotubes react with oxygen and form carbon dioxide, and SnO_2 nanotubes were formed with the escape of carbon dioxide. Due to high temperature and high pressure and alkali, C–C covalent bond in carbon nanotubes broke, resulting in the fracture or defects appearing on the wall, and SnO_2 nanospheres were formed with SnO_2 nuclei attached to these breakage carbon nanotubes. Figure 6 shows the growth schematic diagram of the SnO2 nanotubes.



(a) (b)

(c) (d)

Figure 2: (a) and (b) are SEM images of the as-synthesized SnO_2 nanotubes at different magnification. (c) and (d) are TEM and HRTEM images of the as-synthesized SnO_2 nanotube.



(a) (b)

(c) (d)

Figure 3: SEM images of SnO_2 nanotubes at different dosage of NaOH: (a) 0.4 g, (b) 0.8 g, (c) 1.2 g, (d) 1.6 g.

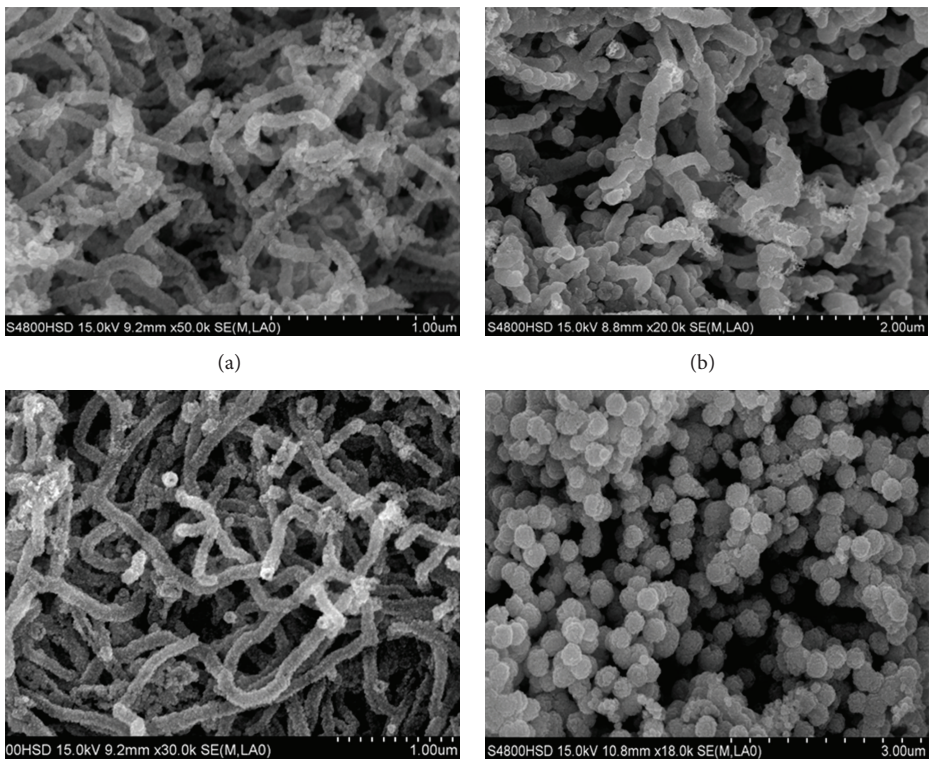


Figure 4: SEM images of SnO_2 nanotubes at different reaction temperatures: (a) 90°C, (b) 120°C, (c) 160°C, (d) 200°C.

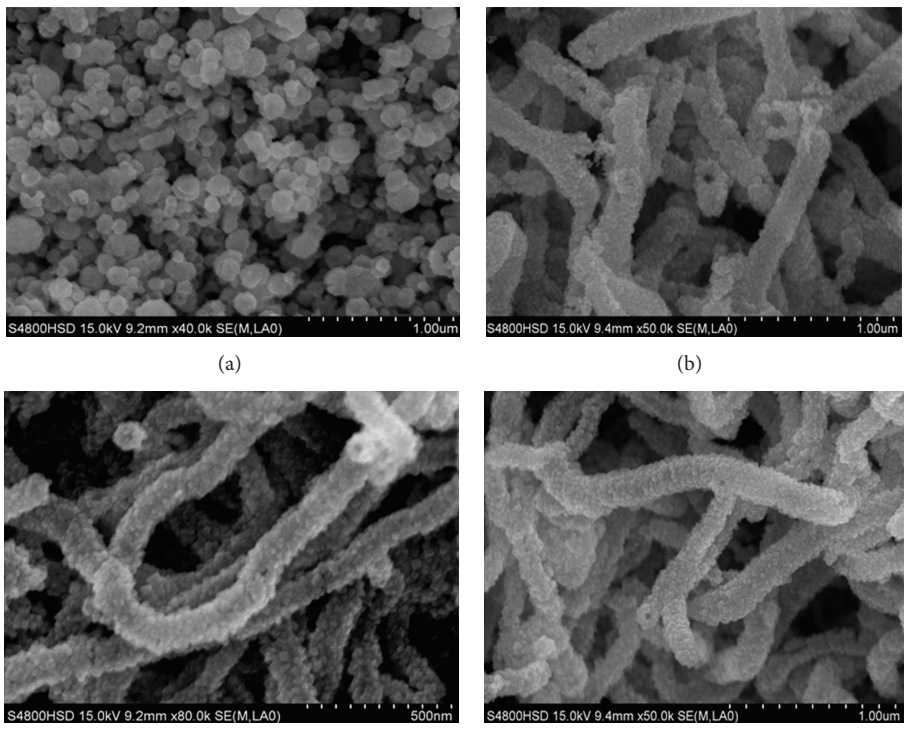


Figure 5: SEM images of SnO_2 nanotubes at different reaction time: (a) 6 h, (b) 10 h, (c) 14 h, (d) 18 h.

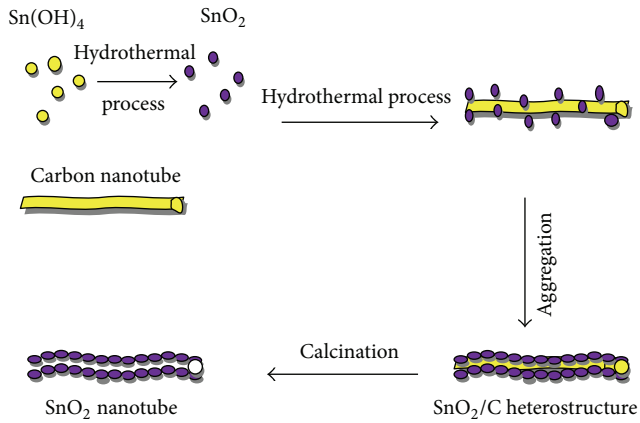


FIGURE 6: Growth schematic of the as-synthesized SnO_2 nanotubes.

4. Conclusion

We report a facile and effective template-induced hydrothermal approach to synthesize the SnO_2 nanotubes at a low temperature. The results indicated that each nanotube is 100 nm in diameter and several micrometers in length and owns a rough surface. Formation mechanism for nanotubes is elucidated based on experimental results.

Acknowledgment

This work was supported by the Program for New Century Excellent Talents in Heilongjiang Provincial University (1252-NCET-018), the Scientific Research Fund of Heilongjiang Provincial Education Department (12531179, 12511144), Doctor Start-up Fund of Harbin Normal University (201213), and Program for Scientific and Technological Innovation Team Construction in Universities of Heilongjiang (no. 2011TD010).

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