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Solution synthesis of ZnO nanotubes via a template-free hydrothermal route

Chunlei Wang, Baodong Mao, Enbo Wang*, Zhenhui Kang, Chungui Tian

Key Laboratory of Polyoxometalate Science of Ministry of Education, Department of Chemistry, Northeast Normal University, Ren Min Street No. 5268, Changchun, Jinlin 130024, PR China

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Abstract

ZnO nanotubes were successfully synthesized by a simple template-free hydrothermal method. X-ray powder diffraction and transmission electron microscopy were used to characterize the as-prepared ZnO nanotubes. The average size of the nanotubes is 200–500 nm in length and 20–30 nm in diameter. In addition, a further investigation of the optimized synthetic conditions has been carried out.

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1. Introduction

The development of the nanodevices depends on the distinct morphology of the materials in a particular way. It is notable that nanotubes have initiated intensive research because a high porosity and large surface area are required to fulfil the demand of high activity in new applications, such as catalysis, intermolecular junctions, storage and release systems [1–4]. Up to now, several kinds of nanotubes, such as sulphides, nitrides and oxides, have been reported [5–7]. Zinc oxide is one of the most important II–VI semiconductor functional materials. The wide direct band gap (3.37 eV) and large exciton binding energy (60 meV) at room temperature make it a potential optoelectronic material in the UV region [8]. Recently, its considerable applications in solar cells, [9] sensors, [10] optoelectonic devices [11] and varistors [12] have also triggered wide research interest. Various ZnO nanostructures such as nanorods [13], nanowires [14], nanobelts [15], nanospings [16], nanocombs [17], nanobridges [18], nanonails [19], nanohelices [20], nanocables [21] and hierarchical nanostructures [22] have been successfully prepared as a consequence.

It is remarkable that tubular ZnO nanostructure, which possesses a different shape with relatively higher surface area, might exhibit some interesting physical and chemical properties unattainable by other nanostructures [23]. However, the research on exploring reasonable synthetic means for the preparation of nanotubular ZnO is comparatively limited. Only several methods including metal-organic chemical vapour deposition [24], thermal evaporation [25], aqueous solution deposition [26], and template-based growth have been employed till now [27]. Shen et al. prepared large-scale uniform ZnO nanotubes arrays via a simple template-based chemical vapor deposition (CVD) method [23]. Han's group reported the low-temperature synthesis of hexagonal ZnO nanotube arrays, which can be formed on zinc foils [27]. Hu et al. prepared ZnO nanotubes by thermal evaporation of the Zn core of the Zn/ZnO nanocables during the annealing process [28]. Xie et al. used the microwave plasma system to fabricate ZnO nanotubes with various dimensions in high yield [29]. Although most of these methods have successfully prepared nanotube arrays or microtubes, the assistance of templates or use of precursors is needed in most of these cases. The difficulty of removing the templates from the final products limits the effective use of these methods. Moreover, the reports on isolated, single-crystalline ZnO nanotubes are less common and the growth of isolated ZnO nanotubes in aqueous solutions still remains a challenge.

Recently, the hydrothermal method has been proved to be attractive as an optional procedure because of its low

* Corresponding author. Tel.: +86 431 85098787; fax: +86 431 85098787.
E-mail addresses: wangenbo@public.cc.jl.cn, wangeb889@nenu.edu.cn (E. Wang).

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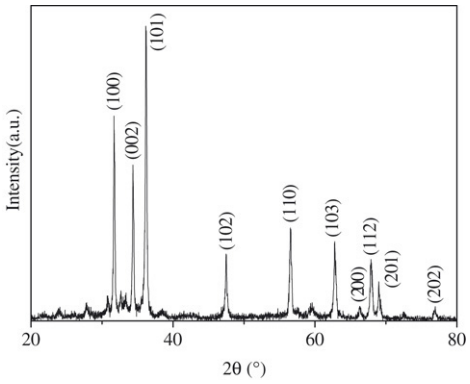

Fig. 1. XRD patterns of the obtained ZnO nanotubes.

growth temperatures and simple process control [30], and many fascinating nanostructures have been prepared depending on it [31–34].

In the present work, we developed a convenient hydrothermal approach for the synthesis of ZnO nanotubes, and this process is repeatable and simply manipulated.

2. Experimental process

All chemicals (analytical grade reagents) were purchased from Beijing Chemicals Co. Ltd. and used as received without further purification. The zinc oxide powders are weighed and ground for about 5 min in a mortar agate for further reaction. Typically, 10 mL hydrogen peroxide (H_2O_2) and 0.2 g zinc oxide powders were placed into a 12 mL Teflon-lined autoclave. The autoclave was sealed and maintained at 180 °C for 24 h and then allowed to cool to room temperature. The white precipitates at the bottom of the autoclave were washed with distilled water and then with absolute ethanol several times. Finally, the precipitates were dried under vacuum at 60 °C for 4 h.

Dry powder samples were used for the structural measurements with a powder X-ray diffractmeter (PXRD, Rigaku, D/max-2500, Cu Kα radiation). The size and morphology of ZnO nanotubes were characterized with transmission electron microscope (TEM, JEM-2010) with an acceleration voltage of 200 kV. A small drop of the powdered sample redispersed by ethanol was deposited on a carbon film coated copper grid purchased commercially and then dried in the air for TEM characterization.

3. Results and discussions

Fig. 1 shows the PXRD patterns of the as-obtained nanotubes. All the obtained ZnO samples are of wurtzite structure (hexagonal phase, space group $P6_3mc$). All the diffraction peaks can be well indexed to the hexagonal phase ZnO reported in JCDDS card (No. 36-1451, $a = 3.249$ Å, $c = 5.206$ Å). The results indicate that the products consist of pure phases and no characteristic peaks were observed for other impurities. The sharp peaks indicate that the products were well crystallized.

The size and morphology of ZnO nanotubes were characterized with transmission electron microscope (TEM).

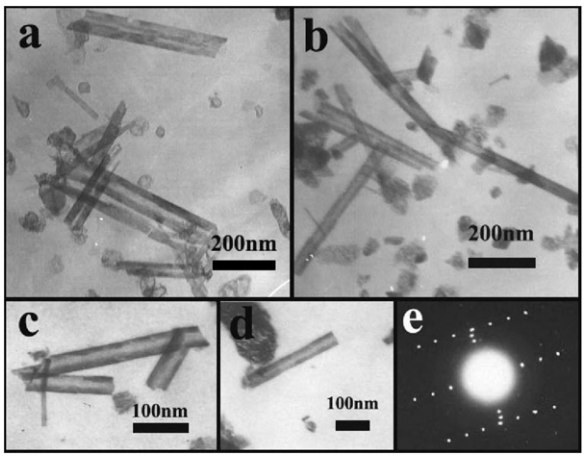

Fig. 2. TEM images of the morphology of as-prepared ZnO nanotubes with (a) reaction time exceeded 24 h; (b) reaction time exceeded 48 h; three typical ZnO nanotubes in (c) high magnification; a single ZnO nanotube in (d) high magnification; (e) the ED image of the as-prepared ZnO nanotubes.

Typical TEM images of the as-prepared ZnO nanotubes are shown in Fig. 2. Fig. 2(a) and (b) shows the as-obtained nanotubes synthesized in aqueous solutions with the diameters about 20–30 nm and reveals that the nanotubes have lengths up to several hundred nanometers. In order to further prove the single crystalline phase of the nanotubes, other two figures of the nanotubes with more dispersed individual are displayed in Fig. 2(c), (d) and the SAED of the nanotubes are displayed in Fig. 2(e). The wall and the inside of the nanotubes are clearly distinguished in the TEM images. The SAED pattern (Fig. 2(e)) indicates that all the ZnO nanotubes are single crystalline. Furthermore, each tube has a uniform diameter along its entire length, indicating the growth anisotropy in the $+c$ axis is strictly maintained throughout the process. It was found that the sizes of the nanotubes increase as the reaction time prolongs, which can be proved by the TEM images of samples prepared in different reaction time. Fig. 3 is the typical images of the obtained nanotubes at the initiative stage of the reactions. When the reaction time reached 5 h, the ZnO nanotubes with average length of about 100 nm (Fig. 3(a), (b)). When the reaction time reached 15 h, as shown in Fig. 3(c), (d), it can be seen that the average length of the nanotubes reached 200 nm. Furthermore, when the reaction time is long enough, the prolongation of the nanotubes become obvious. The nanotubes with length of about 400 nm were obtained when the reaction time exceeded 24 h (Fig. 2(a)) and with length of about 500 nm when the reaction time exceeded 48 h (Fig. 2(b)). On the other hand, the diameter and wall thickness of the nanotubes have not obviously changed during this reaction process. Moreover, the crystalline maturity of the nanotubes depends on, at least partly, the reaction time. Based on the above discussion, the optimized reaction time for the formation of the nanotubes is 48 h as shown in Table 1 (given in bold). In addition, due to the using of the ZnO powders and H_2O_2 as raw materials, obtained products were composed of pure phase ZnO and need to be washed only once to further characterization.

Detailed experimental results also indicate that the existence of H_2O_2 plays a crucial role in the formation of the ZnO