Volume 40, issue 4 February 2008 ISSN 1386-9477

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Physica E 40 (2008) 924–928
PHYSICA E
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Synthesis and characterization of ZnO nanorods by a simple single-source hydrothermal method

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Received 11 September 2007; received in revised form 17 November 2007; accepted 19 November 2007
Available online 8 January 2008

Abstract

By using $Zn(acac)_2 \cdot H_2O$ as a single-source precursor, ZnO nanorods have been synthesized *via* a simple hydrothermal method in the presence of surfactant. The nanorods with an average diameter of 100 nm and a length up to 5 μm were characterized by X-ray diffraction (XRD), energy-dispersive spectroscopy (EDS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), selected-area electron diffraction (SAED), and UV–vis spectrum. It was revealed that the surfactant and the reaction temperature have a great influence on the morphology of the resulting ZnO products.

PACS: 68.65.+g; 81.15.Gh; 61.82.RX

Keywords: Zinc oxide; Nanorods; Single-source precursor; Hydrothermal; Synthesis

1. Introduction

One-dimensional (1D) nanostructured ZnO materials, such as nanorods, nanowires, nanotubes, and nanobelts, have recently stimulated great interest due to their importance in basic scientific research and potential applications in numerous areas such as nanoscale electronics and photonics [1–4]. Generally, 1D ZnO nanostructures can be prepared by various methods including vapor phase growth [5], vapor–liquid–solid (VLS) process [6–9], soft chemical method [10–14], electrophoretic deposition [15–17], thermal evaporation [18,19], sol–gel process [20], metal-organic vapor epitaxy (MOVPE) [21], hydrothermal method [22–24], etc. We are interested in the preparation of nanocrystals using a single-source precursor by a hydrothermal method. This idea is based on the following two reasons. Firstly, nowadays, there is obviously an increased emphasis on the topic of green chemistry and chemical processes [25–29], which aim at the total elimination or at least the minimization of generated waste and the implementation of sustainable processes. We anticipate searching for more "green" or environmentally benign chemical processes. From the viewpoint of green chemistry, reducing the amounts of organic solvents and hazardous substances is highly demanded. A single-source hydrothermal method is a good candidate since the reaction can proceed at a low temperature in H_2O under a sealed environment. Secondly, it is very easy for this method to control reaction conditions. Compared with wet chemical and CVD methods, this method is simple, nonpolluting, and energy economical. Compared with the solvothermal method, the hydrothermal method consumed much less quantities of organic species. To our knowledge, there is no report on the hydrothermal synthesis of ZnO nanorods using $Zn(acac)_2 \cdot H_2O$ as a single-source precursor. The use of $Zn(acac)_2 \cdot H_2O$ as a single-source precursor to ZnO has some advantages: no toxicity, free of pollution and no unwanted by-products to the target products. In this paper, we report on the simple and efficient single-source hydrothermal method for fabrication of ZnO nanorods, and the influence of the surfactant and reaction temperature on ZnO nanocrystals is discussed.

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doi:10.1016/j.physe.2007.11.024

2. Experimental

All chemicals were reagent grade and used without further purification. The precursor $Zn(acac)_2 \cdot H_2O$ was synthesized according to the method literature in Ref. [30]. In a typical synthesis, 0.225 g of the precursor $Zn(acac)_2 \cdot H_2O$ and 0.1 g of a surfactant [polyvinyl alcohol (PVA), polyethylene glycol (PEG), sodium dodecyl sulfate (SDS) or cetyltrimethyl ammonium bromide (CTAB)] were first transferred into a Teflon-lined stainless steel autoclave of 30 mL capacity, then 25 mL of the distilled water was added with vigorous stirring. The autoclave was sealed and maintained at a temperature (130, 150, or 180 °C) in an oven for 5 h. After the autoclave was allowed to cool to room temperature naturally, the resulting mixture was centrifuged, and the precipitate was thoroughly washed with distilled water and ethanol for three times, respectively, and dried at 50 °C for 8 h.

The phase of as-synthesized products was characterized using X-ray diffraction (XRD, Shimadzu XRD-6000) with Cu Kα radiation ($\lambda = 1.5406$ Å) at a scanning rate of $4^\circ\,min^{-1}$. X-ray tubes were operated with electric current of 30 mA and voltage of 40 kV. The morphology and the size of the products were examined by scanning electron microscopy (SEM, JSM-6480) and transmission electron microscopy (TEM, JEM-200CX). Samples for TEM were prepared by dropping the products on a carbon-coated copper grid after ultrasonic dispersing in absolute ethanol. The UV–vis absorption spectrum was investigated on a UV-3010 UV–vis spectrophotometer by dispersing the products in the glycerol/distilled water (1:1) mixture at room temperature with a scanning wavelength range of 300–850 nm. In the UV–vis measurement, a deuterium discharge tube (190–350 nm) and a tungsten iodine lamp with a power of 50 W were used as the incoming light source.

3. Results and discussion

A systematic investigation on the synthesis of ZnO nanocrystals has been made by changing the surfactant and the reaction temperature as mentioned in Section 2. The XRD indicates that all the products synthesized under varied conditions are hexagonal wurtzite ZnO. Fig. 1 shows typical XRD pattern and energy-dispersive spectroscopy (EDS) spectrum of the ZnO nanorods synthesized at 180 °C for 5 h using PVA as a surfactant. The XRD pattern (Fig. 1(a)) reveals that all of the peaks can be indexed to hexagonal wurtzite ZnO (JCPDS 36-1451) with lattice constants $a = 3.25$ Å and $c = 5.20$ Å, and no diffraction peaks arising from any impurities can be detected. The EDS spectrum (Fig. 1(b)) confirms that the nanorods are composed of zinc and oxygen elements, in which the Au peak originates from the gold-sputtered sample for SEM measurement. The result indicates that the as-synthesized ZnO nanorods are highly pure, which is in agreement with the XRD result.

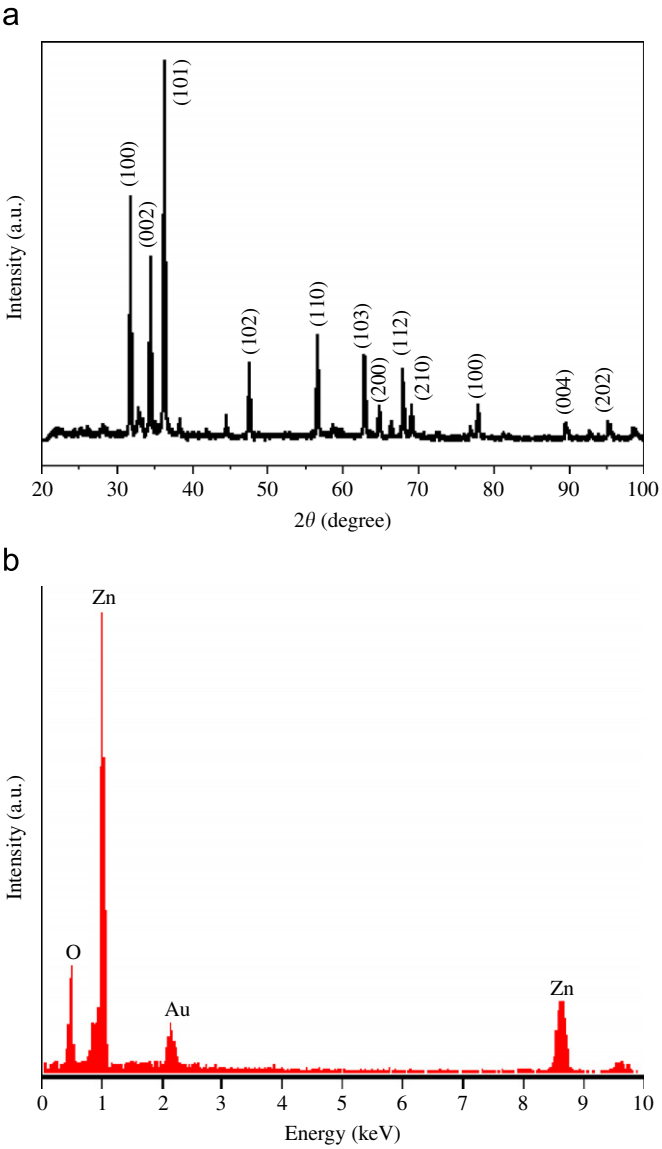

Fig. 1. (a) XRD pattern and (b) EDS spectrum of the ZnO nanorods synthesized at 180 °C for 5 h using PVA as a surfactant.

Fig. 2 shows the effect of the surfactant on the morphology of the products synthesized at 180 °C for 5 h. It can be seen that when using PVA as a surfactant, the products are regular nanorods with an average diameter of 100 nm and lengths in the range of 3–5 μm (Fig. 2(a)). When using PEG, SDS, and CTAB as a surfactant, respectively, all the products are of irregular shapes with a wide size distribution although some of them show rod-like structure (Fig. 2(b)–(d)). Therefore, it is obvious that the surfactant has great influence on the morphology and size of the ZnO products.

The morphology and structure of the ZnO nanorods synthesized at 180 °C for 5 h using PVA as a surfactant have been characterized in further detail using TEM and selected-area electron diffraction (SAED). As shown in Fig. 3(a), the ZnO nanorods are straight and have an average diameter of 100 nm along their whole lengths up to

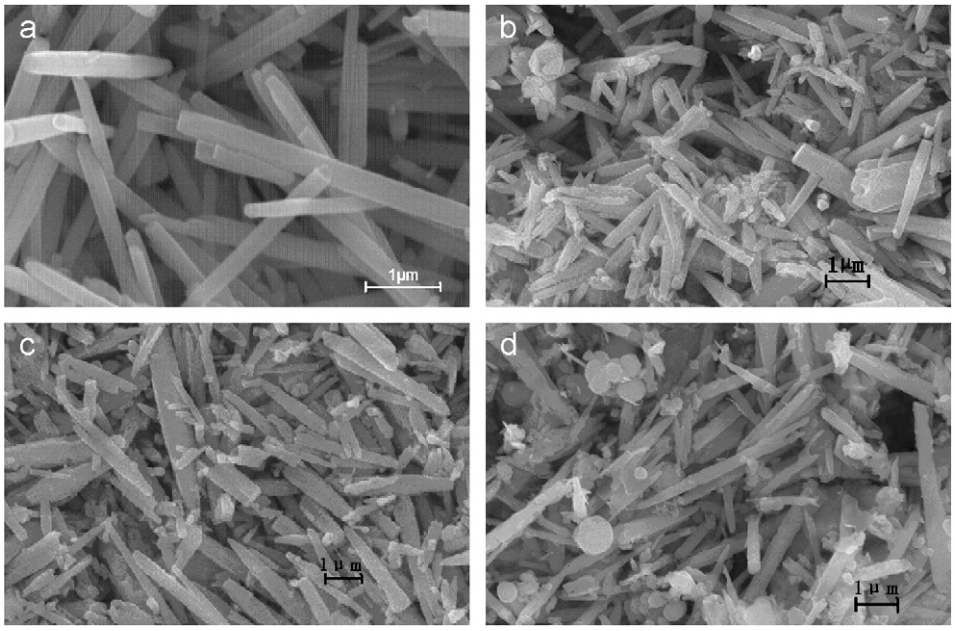

Fig. 2. SEM images of the products synthesized at 180 °C for 5 h with different surfactants: (a) PVA; (b) PEG; (c) SDS; and (d) CTAB.

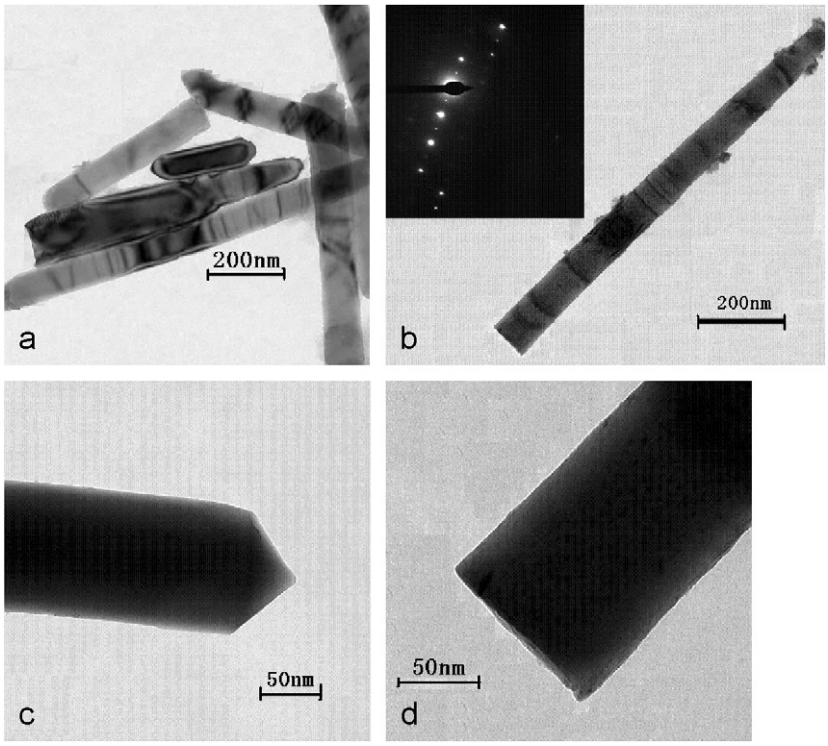

Fig. 3. TEM images and SAED pattern of the ZnO nanorods. (a) TEM image of the ZnO nanorods. (b) TEM image of a typical ZnO nanorod; inset is a SAED pattern. (c) and (d) TEM images showing the different ends of ZnO nanorods.

5 μm, which is consistent with the size observed by SEM. Fig. 3(b) shows a TEM image of a single ZnO nanorod. The SAED pattern (inset in Fig. 3(b)) implies that the as-obtained ZnO nanorods exhibit a single-crystal structure. It is interesting to notice that there are two different kinds of ends in the nanorods: some ends are conical, and other ones are flat (Fig. 3(c),(d)).

The effect of the reaction temperature on the morphology of the products was also investigated. Fig. 4 shows the SEM images of the products synthesized at different reaction temperature for 5 h with PVA as a surfactant. It can be seen that when the reaction proceeded at 130 °C, the products are composed of cubes, spheres, and other irregular shapes with a wide size distribution (Fig. 4(a)).

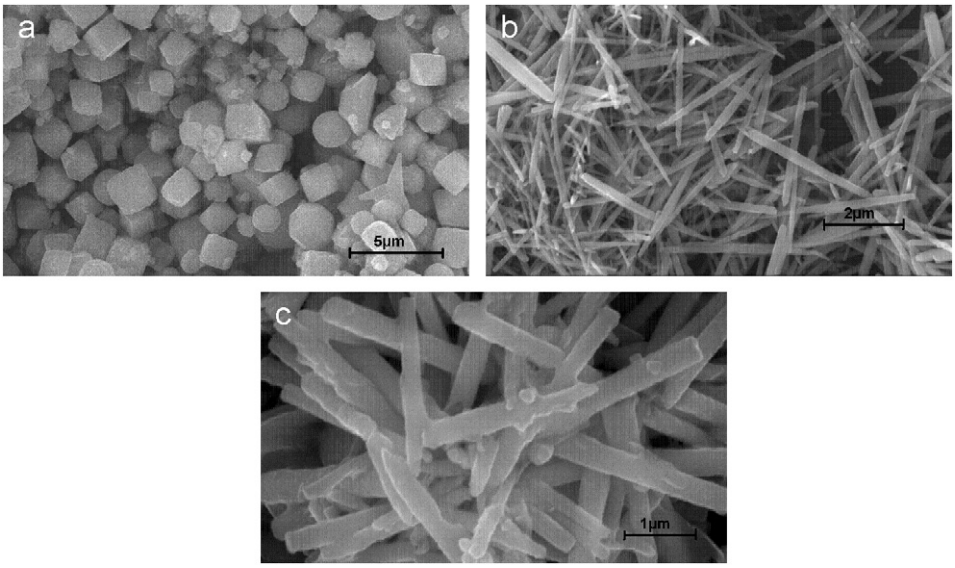

Fig. 4. SEM images of the products synthesized at different reaction temperature for 5 h with PVA as a surfactant: (a) 130 °C; (b) 150 °C; and (c) 180 °C.

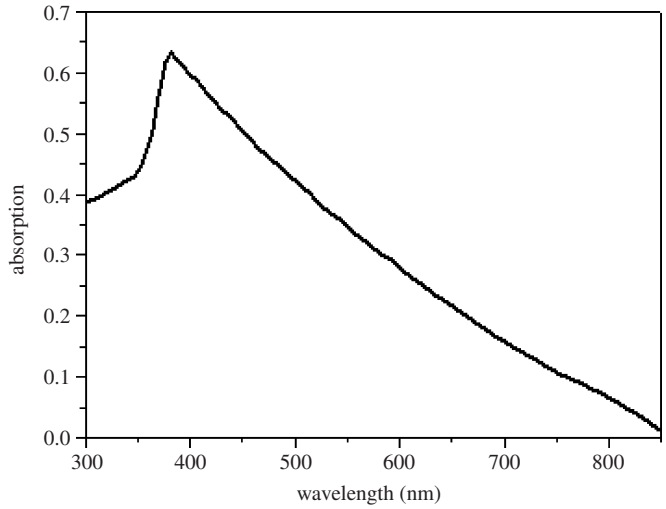

Fig. 5. UV–vis absorption spectrum of the ZnO nanorods synthesized at 180 °C for 5 h using PVA as a surfactant.

By increasing the reaction temperature to 150 °C, the products show needle-like structure (Fig. 4(b)). Upon further increasing the reaction temperature to 180 °C, straight and uniform ZnO nanorods with an average diameter of 100 nm and a length up to 5 μm were obtained (Fig. 4(c)). Thus, the reaction temperature plays an important role in the morphology of the ZnO products.

The UV–vis absorption spectrum of the ZnO nanorods at room temperature is given in Fig. 5. The shown spectrum is corrected for the solvent contribution. The absorption spectrum shows a well-defined exciton band at 381 nm and red-shifted relative to the bulk exciton absorption (373 nm) [31]. The band edge absorption begins with the wavelength at ~800 nm. The interesting light absorption in the visible spectral range suggests that more absorption states or defect energy bands exist in the ZnO nanorods, which maybe related to the specific hydrothermal condition in the synthesis of ZnO nanorods. The as-prepared ZnO nanorods may be good candidate for visible-light photocatalysis materials from the viewpoint of practical applications as a result of their good light absorption in visible light as well as partial ultraviolet light.

4. Conclusions

In summary, ZnO nanorods have been synthesized through a simple hydrothermal method with $Zn(acac)_2 \cdot H_2O$ as a single-source precursor. The nanorods with an average diameter of 100 nm and a length up to 5 μm. The effect of the surfactant and the reaction temperature on the morphology of the resulting ZnO products is investigated. The optical adsorption properties of ZnO nanorods may be very interesting for further application on catalyst. The proposed single-source hydrothermal method to ZnO nanorods was simple, cheap, efficient, and free of pollution, which makes it very suitable for scale-up production. Furthermore, it is well expected that such a technique would be extended to prepare many other important semiconducting metal oxide nanorods.

Acknowledgments

Thanks for financial support from the Natural Science Foundation of Jiangsu Province (no. 04KJB150004) and Social Development Project of Zhenjiang City (SH2006074).

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