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A Simple Refluxing Route to Synthesize of Hexagonal ZnO Nanorods and their Optical Properties†

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Zinc oxide nanorods with hexagonal cross section were prepared through a simple refluxing method in a one-pot aqueous solution. The as-prepared products are characterized by X-ray diffraction, field-emission scanning electron microscopy, UV-visible absorption spectrum and photoluminescence spectrum. The growth process of ZnO nanorods was simply investigated. The diameters of ZnO nanorods are in the range of 80-230 nm and the lengths are estimated to be 2.5-3.0 μm. UV-visible absorption spectrum indicates that the synthesized ZnO nanorods have weak quantum size effects. According to its photoluminescence spectrum obtained with an excitation wavelength of 325 nm, the main emission band of as-prepared ZnO nanorods is located at 403 nm.

Keywords: Zinc oxide, Nanorods, Crystal growth, Optical property.

INTRODUCTION

Recently, one-dimensional (1D) nanocrystals have received considerable attention because of their special properties differing from those of the bulk or spherical nanoparticles. Zinc oxide has been recognized as one of the most promising nanomaterials due to its wide band gap of 3.37 eV and large exciton binding energy of 60 meV [1]. Zinc oxide nanomaterials have potential applications such as UV/visible photodetectors[2], gas sensors[3], luminescent light emitters[4] and solar cells[5]. Up to now, various methods have been applied to prepare one-dimensional (1D) ZnO nanomaterials, such as thermal evaporation[6], metallorganic vapor-phase epitaxy[7], hydrothermal technology[8], chemical vapour deposition[9], microwave and ultrasonic irradiation[10,11]. In spite of much progress, it is still a great challenge for searching a feasible and operable method to synthesis 1D ZnO nanomaterials. In this work, we provide a convenient refluxing route to synthesize ZnO nanorods. The optical property of as-prepared ZnO nanorods was investigated by using UV-visible technology and photoluminescence (PL) spectrum at room temperature.

EXPERIMENTAL

General procedure: In a typical procedure, 0.2 g $Zn(NO_3)_2·6H_2O$, 1.0 g urea and 0.1 g PVP was dissolved in 60 mL distilled water under magnetic stirring. Then, the chemical reaction was carried out for 2 h under fully refluxing conditions (the boiling point of water is 100 ºC). After cooling down to room temperature and standing overnight, the white precipitate was filtered out, washed several times with anhydrous ethanol and distilled water and then dried in a vacuum at 60 ºC for 6-8 h.

Detection method: The phase purity of as-synthesized products was examined by X-ray diffraction (XRD) using a Dandong Y-2000 X-ray diffractometer equipped with graphite monochromatized CuK_α radiation (λ = 1.54178 Å). Field-emission scanning electron microscope (FESEM) images of the samples were taken on a field-emission microscope (Sirion 200, 15 kV) attached with the energy dispersive X-ray spectrometry (EDX). UV-Visible spectrum was obtained on a UV-5550PC spectrophotometer. Photoluminescence (PL) spectrum was recorded on a spectrofluorometer (F-4600).

RESULTS AND DISCUSSION

X-Ray diffraction technology was used to characterize the crystal structure and purity of as-prepared products shown in Fig. 1. The six diffraction peaks of products can be readily indexed to (100), (002), (101), (102), (110), (103), (200), (112), (201) crystal planes of hexagonal ZnO, in good agreement with the reported data for ZnO (a = 3.249 Å, c = 5.205 Å, JCPDS card, No. 05-664). No characteristic peaks were detected for the other impurities such as $Zn(OH)_2$, $ZnCO_3$, *etc*.

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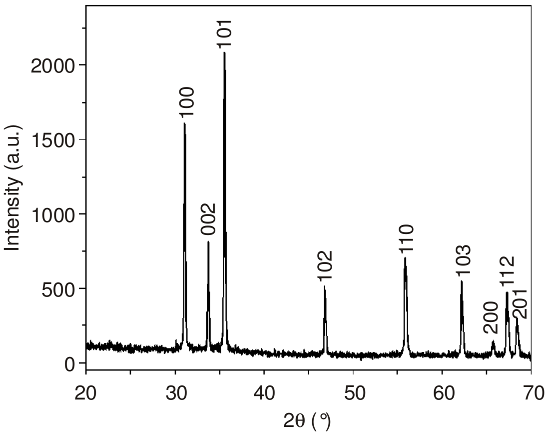

Fig. 1. XRD pattern of as-prepared ZnO nanorods

The strong and sharp diffraction peaks suggest the good crystallinity of as-prepared ZnO nanorods.

The morphology of as-prepared ZnO was detected on a field-emission microscope. Fig. 2 displays the FESEM images of ZnO products obtained through a convenient refluxing method in the aqueous solution. Fig. 2 (a) is the low-magnification image and Fig. 2 (b) is the high-magnification one. Large quantities of one dimensional (1D) hexagonal nanorods are found in the products. These single-crystal nanorods are comparatively uniform and the surfaces of them are fairly smooth. The diameters of ZnO nanorods are in the range of 80-230 nm and the lengths of nanorods are estimated to be 2.5-3mm. By carefully analyzing the FESEM image, it is found that the cross section of an individual nanorod is hexagonal (enlarged image in Fig. 2(b)), which is closely related to the internal structure of hexagonal ZnO crystal.

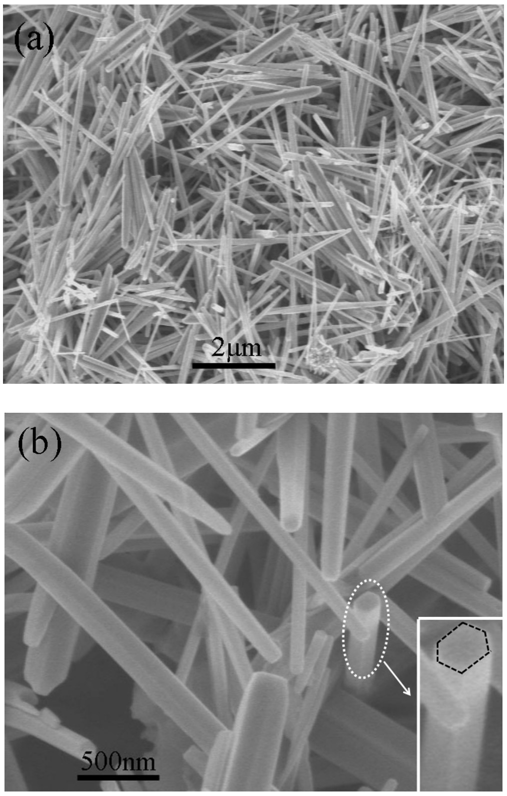

Fig. 2. FESEM images of as-prepared ZnO nanorods

It is well known that ZnO is a polar hexagonal and highly anisotropic crystal with its oriented growth direction along c-axis[12]. In the present synthetic system, the main reaction equations of the ZnO nanorods are proposed as follows:

$$CO(NH_2)_2 + H_2O \rightarrow CO_2 + 2NH_3 \quad (1)$$

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \quad (2)$$

$$Zn^{2+} + 4OH^- \rightarrow Zn(OH)_4^{2-} \quad (3)$$

$$Zn(OH)_4^{2-} \rightarrow ZnO + H_2O + 2OH^- \quad (4)$$

First, urea tempestuously can hydrolyze and produce OH^- ions under refluxing conditions (eqns. 1 and 2). Newly-produced OH^- immediately combine with Zn^{2+} in the solution to generate $Zn(OH)_4^{2-}$ growth units (eqn. 3). Then, The growth units of $Zn(OH)_4^{2-}$ promptly decompose and generate much more ZnO nuclei under heating (eqn. 3). After the nucleation step, ZnO crystal nuclei grow along one-dimensional (1D) direction due to its internal structure. The $Zn(OH)_4^{2-}$ growth units are ceaselessly incorporated into ZnO crystal lattice along *c*-axis. Finally, the elegant hexagonal ZnO nanorods are formed with the prolongation of reaction time. The schematic diagram for the growth process of as-prepared ZnO nanorods may be described in Fig. 3.

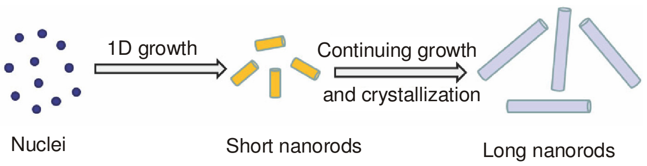

Fig. 3. Schematic diagram for the growth process of as-prepared ZnO nanorods

The optical property of as-prepared ZnO nanorods was investigated by using UV-visible technology and photoluminescence (PL) spectrum at room temperature. Fig. 4(a) shows the UV-visible absorption spectrum of ZnO nanorods. A strong and sharp peak centered at 369 nm in ultraviolet region is clearly observed, which is slightly blue shifted compared to the absorption of bulk ZnO (375 nm). The blue shift may be attributed to the weak quantum size effects of the ZnO nanorods. Fig. 4(b) is the room photoluminescence spectrum of as-prepared ZnO nanorods with an excitation wavelength of 325 nm. The main emission band is located at 403 nm, which is red shifted compared to the ultraviolet emission (excition emission) of bulk ZnO (380 nm). The reason of red shifting is not clear and deserved to be further investigated. The shoulder peak at 468 nm may be attributed to the singly ionized oxygen vacancies and its recombination with a photo-generated hole.

Conclusion

A simple refluxing method was provided to controllably prepare ZnO hexagonal nanorods. The as-obtained ZnO single-crystal nanorods are comparatively uniform and the surfaces of them are fairly smooth. The diameters of these hexagonal nanorods are in the range of 80-230 nm and the lengths are estimated to be 2.5-3.0 mm. The growth process of ZnO nanorod was largely related to its internal crystal structure. The optical property of as-prepared ZnO nanorods was investigated by using UV-visible technology and photoluminescence spectrum at room temperature. The present method is simple, operable and suitable for industrial production.

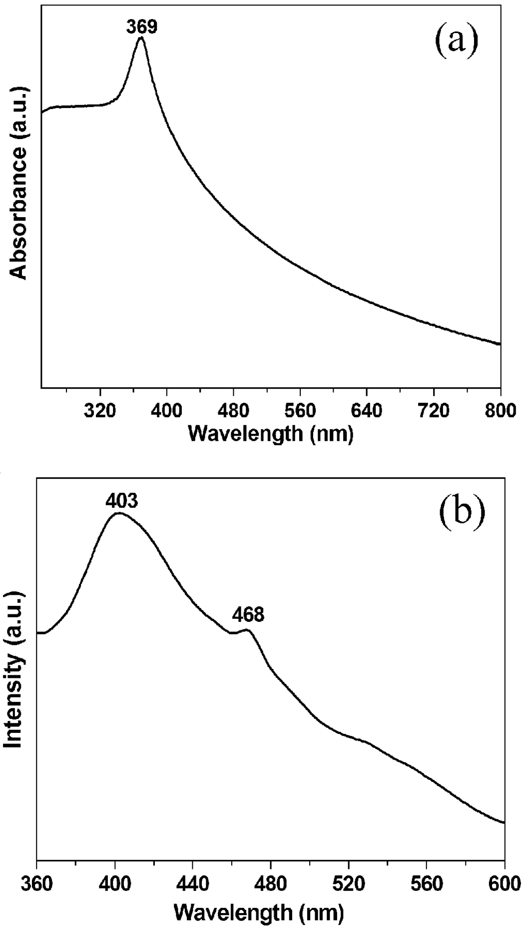

Fig. 4. (a) UV-visible absorption spectrum and (b) photoluminescence spectrum of as-prepared ZnO nanorods

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