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Preparation of ZnO Nanorods and optical characterizations

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Abstract

Single crystalline ZnO nanorods have been prepared by hydrothermal method with synthesized $ZnCl_2 \cdot 4Zn(OH)_2$ as precursors. Morphologies of the nanorods were controlled by various reaction conditions with cetyltrimethylammonium bromide (CTAB) as modifying agent. The nanorods were characterized by techniques such as XRD, TEM, UV–Vis spectra, IR and PL spectra. Microstructure of holes in nanosize was observed on the surface of the nanorod. The UV–Vis spectra indicated that the as-prepared ZnO nanorods have absorption of visible light as well as ultraviolet light. Therefore, these nanorods may be good candidate for visible-light photocatalysis materials from the viewpoint of practical applications. The reason for visible-light absorption was discussed. The photoluminescence property of the nanorod was also investigated.

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1. Introduction

ZnO is a wide band gap semiconductor with an energy gap of 3.37 eV at room temperature. It is a versatile material and has been used considerably for its catalytic, electrical, optoelectronic and photochemical properties [1–4]. ZnO has large exciton binding energy (60 meV) which allows UV lasing action to occur even at room temperature [5] and ZnO with oxygen vacancies (ZnO:Zn) exhibits an efficient green emission. Recently, one-dimensional (1D) nanoscale materials have received considerable attention due to the remarkable properties applied in optoelectronic and electronic nanomaterials. ZnO 1D nanomaterials such as nanorods and nanowires have been intensively investigated for their notable properties [6–9]. Among them, most of the literature reported the photoluminescence (PL) properties with UV emission and few are dedicated to fabricate nanorods with visible absorption. The ZnO semiconductor used as photocatalytic degradation materials of environmental pollutants has also been extensively

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studied, because of its advantages in non-toxic nature, low cost and high reactivity. However, such a photocatalytic degradation only proceeds under UV irradiation because of its wide band gap and can only absorb UV light. Therefore, ZnO-based materials capable of visible-light photocatalysis are required [10]. Herein, we report a simple hydrothermal method to synthesize ZnO nanorod with red-shifted optical absorption.

In the literature, many methods have been used to fabricate 1D ZnO nanorods, such as metal-organic vapor-phase epitaxial growth (MOVPE) [11,12], anodic alumina template [13], common thermal evaporation method [14–17] and soft chemical solution method [18]. In the solution hydrothermal method, always alkali solution of $Zn(OH)_4^{2-}$or $Zn(NH_3)_4^{2-}$ was used as precursors [19,20]. In this paper, $ZnCl_2 \cdot 4Zn(OH)_2$ was used as precursors to synthesize ZnO nanorod using the a hydrothermal method and CTAB was used as surfactant and modifying agent. The optical absorption of the ZnO nanorod showed red shift than bulk ZnO powders. We believe that the presented approach is a simple one to synthesize ZnO nanostructures for the practical application of photocatalysis materials. The PL property of the nanorod was also investigated.

2. Experimental

All the chemicals used in this study were of analytical grade and used without further purification. In a typical procedure, 0.5 M $ZnCl_2$ aqueous solution was mixed with diluted ammonia solution slowly stirring until pH = 6.7. After the reaction was completed, the product was aged, centrifugalized, and washed with distilled water and ethanol more than three times. The precursor was obtained by drying the resulting product in air at 60 °C for 10 h.

Appropriate amounts of the prepared precursor powder (0.98 g) were dispersed in 10–20 ml distilled water, then 20 ml CTAB (0.1 M) was added and the pH value is adjusted to 8–10 by diluted ammonia solution or NaOH solution. The mixture was transferred into a Teflon-lined autoclave of 60 ml and pretreated by ultrasonic water bath for 30 min. Then, the autoclave was sealed and hydrothermally heated for 12–24 h at 180 °C. The obtained product was centrifugalized, washed with distilled water and ethanol, and dried.

Powder X-ray diffraction (XRD) was performed on a Bruker D8-advance X-ray diffractometer with Cu Kα ($\lambda = 1.54178$ Å) radiation. Size and morphology of the precursor and the product were determined using a Hitachi model H-800 transmission electron microscope (TEM) performed at 200 kv. Infrared absorption spectroscopy (IR) spectra were measured at room temperature on a FTIR spectrometer (Nicolet 7900) using the KBr Pellet technique to determine the structure of the product. UV–Vis absorption spectra were recorded using a 760 CRT UV–Vis double-beam spectrophotometer with a deuterium discharge tube (190–350 nm) and a tungsten iodine lamp (330–900 nm). The scanning wavelength range is 200–800 nm. PL spectrum was performed at room temperature using a FLS920 fluorescence spectrophotometer with a Xe lamp.

3. Results and discussion

The phase composition of the prepared precursor was determined by XRD techniques. XRD patterns in Fig. 1 shows that all the diffraction peaks are well consistent with the compound $ZnCl_2 \cdot 4Zn(OH)_2$ (JCPDS card No. 7-115). No characteristic peak of other species such as $Zn(OH)_2$ or $ZnCl_2$ was detected. The precursor was fully crystallized. XRD patterns of the as-obtained nanorods are shown in Fig. 2. All the peaks of the nanorods prepared under various conditions can be indexed to the wurtzite ZnO (JCPDS card No. 36-1451, $a = 3.249$ Å and $c = 5.206$ Å) with high crystallinity. No characteristic peak of impurities was detected which means that all the crystalline precursors decomposed and grew into ZnO single crystals. In Fig. 2a, the intensity ratio of (1 0 0) peaks is notably enhanced than in Fig. 2b and c and standard values which means that this ZnO sample oriented grow in (1 0 0) direction. Employing the Scherrer equation, the sizes of the nanorods prepared in the absence of CTAB are also larger than those prepared in the presence of CTAB.