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Original research article

Controlled synthesis of nano-ZnO via hydro/solvothermal process and study of their optical properties

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ABSTRACT

ZnO nanocrystals with different morphologies were successfully synthesized via simple solvothermal method. Zinc acetate was used as a zinc source and sodium decyl sulfate as a structure-directing template. The influence of the solvent (tetrahydrofuran THF) on the morphology and structure was elucidated systematically. The morphology, particle size, crystalline structure and optical properties of the as-prepared ZnO were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), Raman spectroscopy, UV-vis spectroscopy, infrared spectroscopy and photoluminescence (PL). The photoluminescence spectra have identified several kinds of defects in as-synthesized ZnO materials.

1. Introduction

In recent years, studies of transition metal oxides nanostructures have become important due to the different potential applications, such as solar cells (Sönmezoglu et al., 2014), gas sensors [1], optical devices [2], display windows [3], photocatalysts [4] and surface acoustic waveguides [5]. ZnO is a direct wide band gap (3.37 eV) semiconductor with a large excitonic binding energy (60 meV) at room temperature [6]. As it is known, when the particle sizes of many semiconductors decrease to nanometer or sub-nanometer scales, these materials usually exhibit quantum size effects, presenting different electric and optical properties from bulk materials [7].

Considerable efforts have been exerted to prepare distinctive ZnO with various morphologies such as nanowires [8], nanorods [9], naonobelts [10], nanotubes [11] etc. Synthesis of size and shape controlled ZnO nanostructures is very important in controlling their optical and chemical properties. Several methods of synthesizing ZnO materials with different morphologies and structures have been demonstrated, such as sol-gel method [12], hydrothermal synthesis [13–15], chemical vapor deposition (CVD) [16], solvothermal synthesis [17] and thermal evaporation [18]. Hydrothermal synthesis, as an important method of wet chemistry, has attracted growing attention from scientists in general and chemists in particular for its operational simplicity, low cost, high efficiency, as well as its environment-friendly nature which can facilitate a safe large-scale production [19].

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Zinc oxide nanostructures have been synthesized several times using cetyltrimethylammonium bromide (CTAB) and hexamethylenetetramine (HMT) [20]. Liangyuan et al. [21] reported a simpler SDS-assisted hydrothermal process for the synthesis of one-dimensional needle-like ZnO nanorods.

Recently, Razali et al. [22] fabricated ZnO microsphere by solvothermal approach using zinc acetate ($Zn(CH_3COO)_2{\cdot}2H_2O$) as zinc sources, ethanol and diethanolamine (DEA) were used as starting materials. Sarkar et al. [23] prepared the ZnO nanostructures with nanowire morphologies by the solvothermal method. The hexagonal ZnO nanowires are 75 nm wide and about 1.2 μm long.

To the best of our knowledge, the solvothermal synthesis of ZnO nanostructures from zinc acetate and sodium decyl sulfate have never been reported. In this work, the ZnO nanostructures were synthesized using the hydro/solvothermal process. In fact, we report the influence of solvent concentration on formation of ZnO nanostructures via a hydr/solvothermal method using sodium hydroxide as a precipitating agent, zinc acetate and sodium decyl sulfate, which plays an important role in the fabrication of ZnO nanostructures. Moreover, the possible mechanism for the sodium decyl sulfate-assisted solvothermal synthesis of ZnO nanoflakes has been preliminary presented.

2. Experimental section

2.1. Hydro/solvothermal synthesis

All of the chemical reagents were of analytical grade. They were purchased from Acros Organics and used without further purification.

The detailed process for the synthesis was as follows. In a typical synthesis, the preparation was made by mixing zinc acetate (0.0843 g), sodium decyl sulfate (0.1 g), sodium hydroxide (0.107 g) and tetrahydrofuran (5 mL). Reactants were introduced in this order and stirred for 1 h at room temperature before introducing the resulting mixture in a Teflon-lined steel autoclave and the temperature set at 180 °C for 2 h under autogenous pressure. The pH of the reaction mixture remains close to pH ≈ 12 during the whole synthesis. The resulting powder was washed with water and acetone to remove the residues of sodium decyl sulfate and then dried at 80 °C for 4 h. Comparative experiments were carried out to investigate the influence of the reaction time on the formation process of ZnO nanocrystalline.

2.2. Characterization techniques

The X-ray powder diffraction data (XRD) of all samples were obtained on a X'Pert Pro Panalytical diffractometer with CuKα radiation (λ = 1.54056 Å) and graphite monochromator. The XRD measurements were carried out by applying a step-scanning method (2θ ranging from 3° to 70°), the scanning rate is 0.017° s^{-1} and the step time is 1 s. Scanning electron microscopy (SEM) study was recorded on a Cambridge Instruments Stereoscan 120. Fourier-transform infrared spectra (FTIR) were recorded from 4000 to 400 cm^{-1} on a Nicolet 380 spectrometer on pellets of samples dispersed in KBr. Raman spectroscopy was performed using a Jobin Yvon T 64000 spectrometer (blue laser excitation with 488 nm wavelength and <55 mW power at the sample). Transmission electron microscopy (TEM) was carried out with a Philips G20 Ultra-Twin Microscope at an accelerating voltage of 200 kV. One droplet of the powder dispersed in CH_3CH_2OH was deposited onto a carbon-coated copper grid and left to dry in the air. The optical parameters of sample were calculated from the optical absorbance data recorded in the wavelength ranging from 300 to 700 nm using a UV–vis spectrophotometer Shimadzu-3101PC. Photoluminescence (PL) spectroscopy was performed using a 325 mm Jobin Yvon luminescence spectrometer.

3. Results and discussion

3.1. X-ray diffraction

XRD patterns of the samples synthesized with H_2O, THF and commercial ZnO are shown in Fig. 1. In fact, the XRD patterns shown in Fig. 1 indicate that the d-spacing values of all diffraction peaks are identical to those of the hexagonal crystalline phase ZnO with lattice constants of a = b = 3.247 Å and c = 5.200 Å according to the literature values (JCPDS No. 36-1451). The sharp diffraction peaks suggest the good crystallinity of the both samples under the reported conditions. Also, no other peaks related to impurity were detected in the pattern, indicating the purity of both samples.

Then the average crystallite size (L) can be estimated from Scherer's equation [24].

$$L = \frac{0{,}9\ \lambda}{\beta\ \cos\theta}$$

where L is the average crystallite size, λ = 0.15418 nm, β is the half-maximum peak width and θ is the diffraction angle in degrees. The average crystallite size of ZnO nanoflakes is estimated to be 68 nm.