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Synthesis and optical properties of Co-doped ZnO nanofibers prepared by electrospinning

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ABSTRACT

In this work, Co-doped ZnO nanofibers have been fabricated successfully by an electrospinning technique. The as-prepared nanofibers are characterized by themogravimetric analysis (TG), scanning electron microscopy (SEM), transmission electron microscopy (TEM), powder X-ray diffraction (XRD), Raman spectra and photoluminescence spectroscopy (PL). Results have showed that a wurtzite ZnO nanofibers were obtained and the PL spectrum showed a red-shift by 10 nm due to narrowing of the ZnO band gap (~3.29 eV) as a result of Co doping. Meanwhile, Raman scattering spectra exhibited an unusual peak at 540 cm^{-1}.

1. Introduction

Due to its wide direct band gap (3.37 eV) and large exciton binding energy (60 meV), zinc oxide (ZnO) have been explored worldwide for potential application in ultraviolet (UV) light emitters and detectors [1], transparent electrodes solar cells [2], gas sensors [3], and piezoelectric transducers [4]. ZnO based 1D nanostructures including nanowires, nanorods and nanofibers, have also attracted much attention because of its excellent physical properties and potential application in diverse electronic and photonic devices [5]. The electronic and optical properties of ZnO nanostructures are largely dependent on their composition/doping, crystal structure, dimension, and morphology. In particular, doping is a widely used method to change ZnO composition and improve its the electrical, magnetic, and optical properties [6]. Therefore, many researchers have improved the properties of nanosized ZnO by doping, For example, Dole et al. have prepared ZnO nanoparticles by doping Mn in order to study the change in its structure [7]. Liu et al. obtained ZnO powders by doping Fe to improve its structure and magnetic properties [8]. And Soumahoro et al. investigated the influence of Fe doping on structural, optical and magnetic properties of ZnO film [9].

Until now, many methods for fabrication of ZnO nanostructured materials have been developed, ranging from lithographic techniques, molecular beam epitaxial to chemical techniques such as solid–vapor decomposition [10–13]. In comparison to most nanofabrication techniques, electrospinning is currently the one of the most promising technique to produce continuous nanofibers on a large scale and the fiber diameter can be adjusted from nanometers to microns. Also, electrospinning is a relatively easy and fast process to produce ZnO or metal ion doped ZnO nanofibers. Herein, we report the synthesis of Co-doped ZnO nanofibers by an electrospinning technique. The structure, morphology and optical properties of Co-doped ZnO nanofibers have been characterized using themogravimetric analysis (TG), X-ray diffraction (XRD), transmission electron microscopy (TEM), Raman spectra, photoluminescence spectra respectively.

2. Experimental

2.1. Preparation of Co-doped ZnO nanofibers

The Co-doped ZnO nanofibers with dopant concentrations 5 mol% were synthesized by sol–gel based on electrospinning process. In a typical experiment, 2.5 g of PVP (Mw = 50,000) was added to 15 mL alcohol at 25 °C with vigorous stirring for 4 h. A certain amount of zinc acetate ($Zn(CH_3COO)_2$) and cobalt acetate($C_4H_6CoO_4$) were then added to PVP solution with

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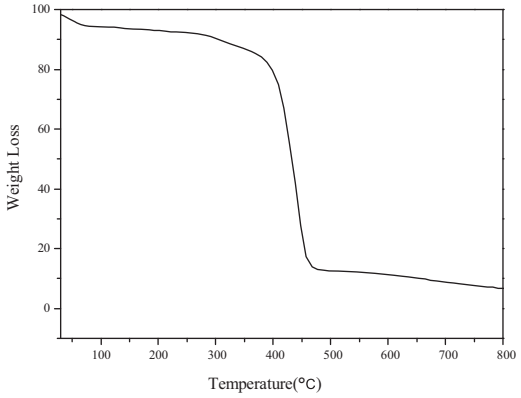

Fig. 1. TG curves of precursor fibers of PVP/zinc acetate/cobalt acetate composite.

vigorous stirring for 2 h to form a viscous gel. The solution was then pumped into a plastic syringe with a 1 mm internal diameter stainless steel needle at a constant flow rate of 0.5 ml/h. A high voltage of 25 kV was supplied at the stainless steel needle by a direct current power supply. A piece of grounded silicon wafer was placed 20 cm below the tip of the needle to collect the nanofibers. The collected electrospun nanofibers were then dried at 125 °C for 6 h. The dried electrospun precursors were then annealed in a furnace at 600 °C for 2 h in air.

2.2. Characterization of Co-doped ZnO nanofibers

Themogravimetric analysis (TG) was performed on a NETZSCH STA 449 C thermo-analyzer in an air atmosphere. For SEM investigation, a Hitach-600 was used. The phase structure of the as-synthesized samples was examined by X-ray diffraction (XRD, D/Max2550VB+/PC, Philips, Holland) with Cu-Kα radiation (λ = 1.5406 Å). Transmission electron microscopy (TEM, JEM-3010, Questar, New Hope, USA) was performed with an acceleration voltage of 300 kV. The Raman spectra (inVia, Renishaw, Gloucestershire, UK) were excited by a 532 cm Nd:YAG laser at room temperature. Its photoluminescence properties were investigated by a spectrometer (Spex. 1404P), using He–Cd laser with excitation wavelength of 325 nm.

3. Results and discussion

3.1. TG of the as-prepared nanofibers

The precursor fibers of PVP/zinc acetate/cobalt acetate composite obtained after electrospinning should be annealed because large amounts of organic polymer and solvent of ethanol are contained

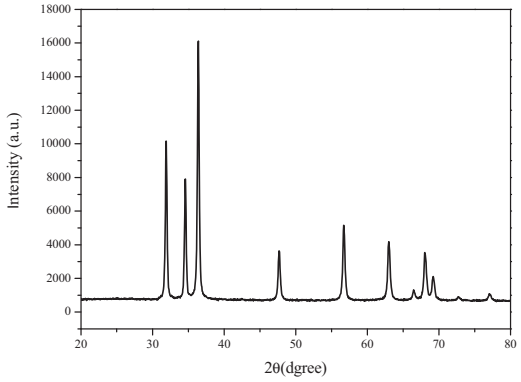

Fig. 2. XRD of Co-doped ZnO nanofibers after calcination at 600 °C.

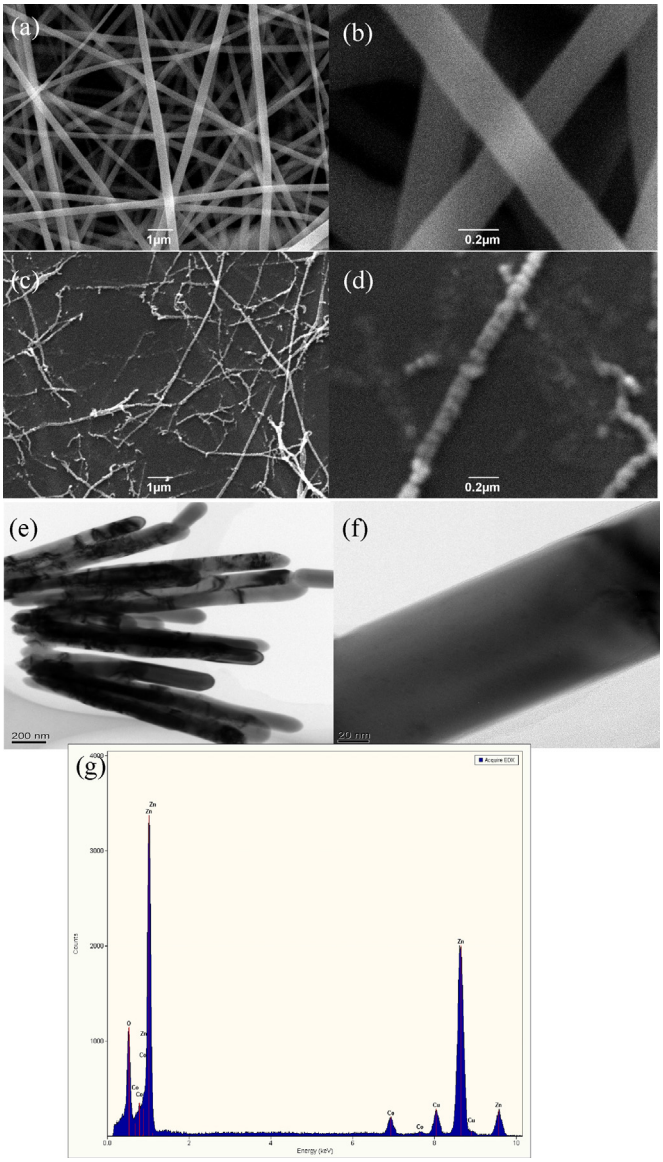

Fig. 3. SEM images of PVP/zinc acetate/cobalt acetate composite nanofibers at (a) low magnification and (b) high magnification and Co-doped ZnO nanofibers at (c) low magnification and (d) high magnification; TEM images of Co-doped ZnO nanofibers at (e) low magnification and (f) high magnification. (g) EDX spectroscopy of the Co-doped ZnO nanofibers.

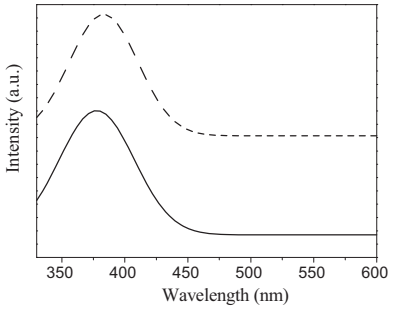

Fig. 4. PL spectures of ZnO nanofibers (solid line) and Co-doped ZnO (dashed line) after calcination at 600 °C.