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

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ABSTRACT

Mg-doped ZnO nanofibers with different doping concentrations have been successfully synthesized by electrospinning method. The nanofibers were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and Raman spectroscopy. The results show that Mg doping has little influence on the diameter and surface morphology of ZnO nanofibers, and the nanofibers are crystalline and exhibit the hexagonal structure. The photoluminescence spectroscopy studies indicate that the ultraviolet emissions present blue shift with increasing Mg doping concentration.

1. Introduction

One-dimensional semiconducting materials have long been a subject of intense research in the area of synthesis, characterization, and novel applications due to their remarkable electrical, optical, and chemical properties [1–3]. Among these nanomaterials, ZnO is one of the most promising materials since it has a high mechanical and thermal stability, a wide band-gap (3.37 eV), and a high free-exciton binding energy (60 meV) [4]. Nanostructured ZnO is widely used in ultraviolet (UV)/blue emission devices, piezoelectric devices, solar cells, chemical sensors, photocatalysis, and field emission [5–8]. Up to now, a number of synthetic methods including electrospinning [9], hydrothermal [10], chemical vapor deposition [11] and electrochemical deposition [12] have been used to prepare ZnO nanomaterials such as nanofibers, nanowires, and nanorods. Compared with other methods, electrospinning is a simple, versatile and convenient approach for manufacturing one-dimensional nanomaterials with the characteristic of easy control and low cost. This technique has been used to synthesize a wide range of one-dimensional nanomaterials, and the fabricated nanofibers by electrospinning method can have surface area to volume ratio approximately one to two orders of magnitude more than that of continuous thin films [13].

Meanwhile, doping with selective elements offers an effective method to enhance and control the electrical and optical properties of ZnO nanostructures, which is crucial for its practical application. And, ZnO doped with proper elements, such as Li, Al, Mn, and Cr has been studied [14–17]. By alloying with MgO, which has a wider band-gap (7.3 eV) [18], the band-gap of ZnO can be modulated for the realization of light-emitting devices operating in a wider wavelength region. Moreover, since the ionic radii of Mg^{2+} (0.57 Å) and Zn^{2+} (0.60 Å) are quite close, they can alloy by replacing each other in the matrix. Ohotomo et al. reported the preparation of *c*-axis oriented metastable hexagonal Mg-doped ZnO with Mg content up to 33 at.% [19]. Recently, some preparations of Mg-doped ZnO thin films and various nanostructures have been reported [20,21]. However its nanofibers fabricated by electrospinning method have not been investigated yet. In this paper, we report the successful fabrication of Mg-doped ZnO nanofibers with diameters ranging from 50 to 100 nm via electrospinning technique. The effect of Mg doping on the crystal structure, morphology and optical properties of the nanofibers was also investigated.

2. Experimental details

Mg-doped ZnO nanofibers with different doping concentrations were prepared by electrospinning. In a typical procedure, aqueous polyvinyl alcohol (PVA, Mw 80,000) solution (10 wt%) was first prepared by dissolving PVA powder in distilled water and put the mixture aside for 12 h at room temperature and then into a water bath at 80 °C for 4 h, followed by cooling down to room temperature with continuation of stirring for 2 h. Then the solution of zinc acetate (20 wt%) and/or the suitable amount of $Mg(NO_3)_2$ was dropped slowly into the aqueous PVA solution of 10 wt% with stirring, and the reaction proceeded at 50 °C for 1 h. The PVA and the zinc

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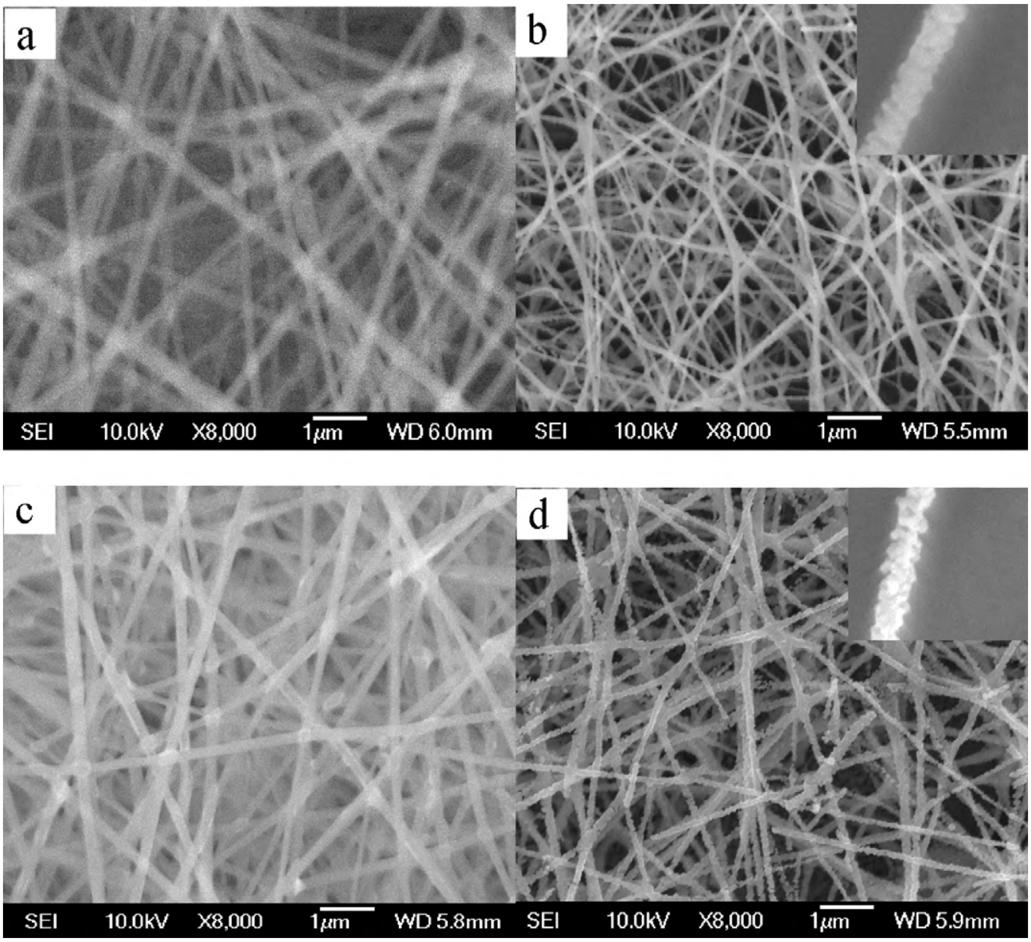

Fig. 1. SEM images of nanofibers: (a) undoped ZnO/PVA composite nanofibers. (b) undoped ZnO nanofibers calcined at 650 °C. (c) 5 at.% Mg-doped ZnO/PVA composite nanofibers. (d) 5 at.% Mg-doped ZnO nanofibers calcined at 650 °C.

acetate was in a weight ratio of 1:1 and the atomic ratio of Mg^{2+} and Zn^{2+} in the precursor solution ranged from 0 to 8 at.%. This mixture was aged at room temperature for 3–6 h, then, a viscous sol solution was obtained to give the final electrospinning solution.

The electrospinning apparatus was consisted of a 20 ml syringe, a syringe needle (ID = 0.5 mm) with flat tip connected with the positive electrode, a grounded cooper plates collector, and a high-voltage supply equipped with voltage digital meter. The precursor solutions were electrospun at a positive voltage of 8 kV, an ambient temperature of 20 °C, and a tip-to-collector distance of 10 cm. The composite fibers were collected on the grounded substrate, and undoped and Mg-doped ZnO nanofibers were finally obtained by calcination at 650 °C for 3 h in air. The morphology and crystal structure were characterized with scanning electron microscopy (SEM) and X-ray diffraction (XRD), respectively. Raman scattering and room temperature photoluminescence (PL) spectroscopy with the Ar^+ (514.5 nm) and He–Cd (325 nm) laser lines as the excitation sources, respectively, were used to examine the optical properties of the nanofibers.

3. Results and discussion

The morphology of the electrospinning nanofibers was studied by scanning electron microscopy (SEM). Fig. 1 shows the SEM images of as-synthesized undoped ZnO/PVA and 5 at.% Mg-doped ZnO/PVA composite nanofibers before and after calcination. In both cases, the samples are composed of uniform nanofibers free of beads. Moreover, the distributions of nanofibers are fairly random with no distinct alignment owing to the bending instability associated with the spinning jet. From Fig. 1(a) and (c), the as-synthesized undoped and Mg-doped composite fibers before calcination have smooth surface because of amorphous ZnO/PVA and polymeric property. They are long than several millimeters, with a diameter of approximate 300 nm. Furthermore, it can be seen that, in contrast to undoped ZnO/PVA composite nanofibers, the diameter of Mg-doped ZnO composite nanofibers is slightly decreased. This may be due to introduction of $Mg(NO_3)_2$, which altered the conductivity and the viscosity slightly. It is well known that the morphology and properties of the electrospun nanofibers are influenced by the viscosity and conductivity of the precursor solution. Thus, the change of the conductivity and viscosity led to thinner diameters of Mg-doped ZnO/PVA composite nanofibers. This is in agreement with the report on Al-doped ZnO nanofibers [22]. After calcinations at 650 °C, the diameters of undoped and Mg-doped ZnO nanofibers shrank drastically to 50–100 nm, as shown in Fig. 1(b) and (d). The shrinkage of nanofibers is due to the removal of PVA from the fibers and the conversion of metal salts to metal oxides. It can also be seen from the inset images of Fig. 1(b) and (d) that the surface of undoped and Mg-doped ZnO nanofibers appears a rough porous structure, and the surface of Mg-doped ZnO nanofibers is a little rougher than the surface of undoped ZnO nanofibers.

Fig. 2 shows the XRD patterns of undoped and 5 at.% Mg-doped ZnO nanofibers. It can be seen that a series of diffraction patterns at 2θ = 31.7, 34.4, 36.2, 47.5, 56.5, 62.8, 66.3, 67.9, 69.0, corresponding to (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (2 0 0), (1 1 2), (2 0 1) of hexagonal wurtzite ZnO. No other phase was observed, which suggests that little Mg doping would not change the crystal structures of ZnO nanofibers. Moreover, no peaks related to Mg element and compounds were found in the sample, which indicates that the Mg doping exists in the form of impurity atoms. In view of the full width at half-maximum (FWHM) of the XRD peaks, the crystallites are

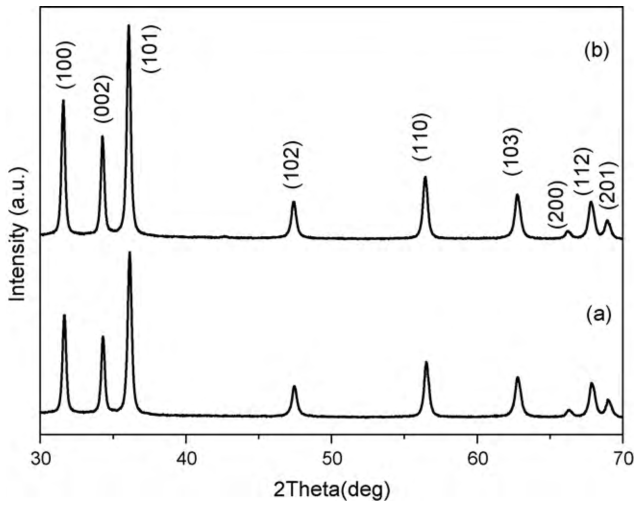

Fig. 2. XRD patterns of undoped (a) and 5 at.% Mg-doped (b) ZnO nanofibers calcined at 650 °C for 3 h.

thought to have high crystallographic quality. Furthermore, both the intensity and the FWHM of diffraction peaks are not sensitive to the Mg doping, demonstrating that no degeneration is brought in the crystallinity of the nanofibers with little Mg doping.

The optical properties of the samples have been investigated by Raman and photoluminescence measurements which were performed at room temperature. Fig. 3 shows the Raman spectra of undoped and 5 at.% Mg-doped ZnO nanofibers in the range of 300–800 cm^{-1}. It can be seen from Fig. 3(a) and (b) that the strong and dominant E_2 (high) mode of ZnO located at 438 cm^{-1} is observed for undoped and 5% Mg-doped ZnO samples, which is the characteristic of the Raman-active mode of wurtzite hexagonal ZnO. Also two very weak and suppressed peaks at 332 and 580 cm^{-1} were also observed in the spectrum and assigned to the E_{2H}–E_{2L} and E_{1L} modes, respectively. And appearance of a very suppressed and short E_{1L} mode suggests that the formation defects (oxygen vacancies or zinc interstitials) [23] or impurities (Mg) existed in the synthesized nanofibers. Raman measurements show that both the undoped and Mg-doped ZnO nanofibers have a good crystal quality with hexagonal wurtzite structure, and little Mg doping does not change the structure of ZnO. This is consistent with the XRD patterns.

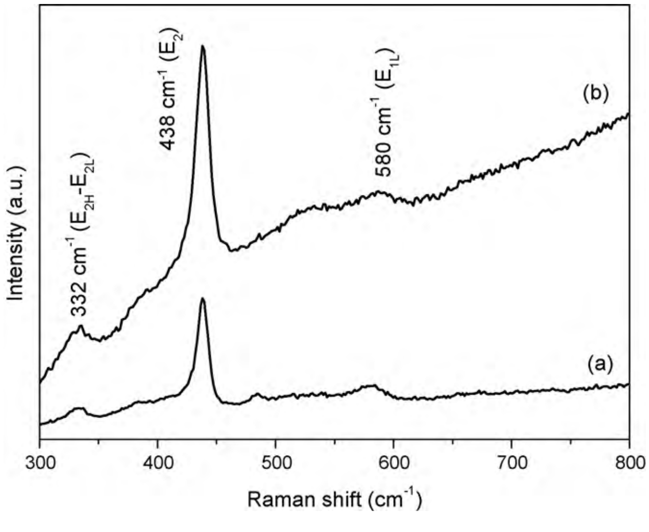

Fig. 3. Raman spectrum of undoped (a) and 5 at.% Mg-doped (b) ZnO nanofibers calcined at 650 °C for 3 h.

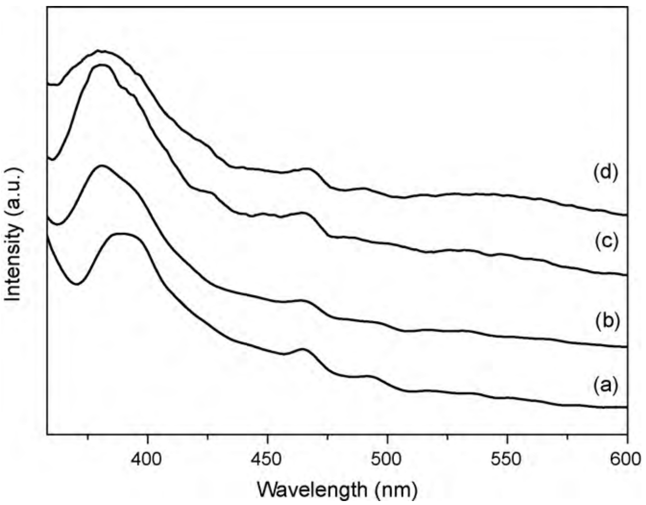

Fig. 4. Room temperature photoluminescence spectrum of Mg-doped ZnO nanofibers with different doping concentration after calcinations: (a) 0, (b) 3, (c) 5, and (d) 8 at.%.

Fig. 4 shows the PL spectrum of undoped and Mg-doped ZnO nanofibers with different doping concentrations at room temperature, the curves (a), (b), (c), (d) correspond to the doping concentration 0, 3, 5 and 8 at.%, respectively. It is very interesting to observe the strong ultraviolet (UV) emission and the weak blue emission (~466 nm) peaks from all four samples. The room temperature UV emissions are usually attributed to free-exciton recombination or the near band edge emission [24]. As can be seen from Fig. 4, with increasing the contents of Mg dopants, the intensity of UV emission was enhanced slightly, and the intensity became strongest when the Mg doping concentration reached 5 at.%. Then the intensity of UV emission gradually decreased with continually increasing the Mg doping concentration. At the same time, with the Mg doping concentration increases from 0, 3, 5 to 8 at.% the ultraviolet emission peak shows a blue shift from 388, 383, 380 to 378 nm because of the modulation of the band-gap caused by Mg substitution, which suggests that the optical band-gap of the Mg-doped ZnO nanofibers can be tunable by changing the Mg concentrations. The blue emissions might attribute to surface defects in ZnO nanofibers [25]. From Fig. 4, the appearance of a strong intensity of UV emission and a weak blue emission from the ZnO nanofibers indicate that the obtained products are good in crystallinity with less structural defects.

4. Conclusions

Mg-doped ZnO nanofibers with different doping concentrations were fabricated using an electrospinning technique. The nanofibers were crystalline and exhibited the hexagonal structure, and little Mg doping would not change the crystal structures of ZnO nanofibers. The SEM measurements indicate that Mg doping has a slight influence the diameter and surface morphology of ZnO nanofibers. Room temperature photoluminescence (PL) spectrum of all samples included two emission peaks: a strong ultraviolet emission and a weak blue emission. The ultraviolet emission peaks presented blue shift with increasing Mg doping concentration.

Acknowledgments

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