

Size control of Co-doped ZnO rods by changing the solvent

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Abstract. In this work, the Co-doped ZnO rods were prepared by the hydrothermal method. The size of these rods can be changed from micro-size to nano-size by using different solutions during the preparation. The results of transmission electron microscopy (TEM) and selected area electron diffraction (SAED) showed that the as-prepared nano-sized Co-doped rods have single-crystal structure. The polarized Raman experiments were presented on an individual micro-sized Co-doped ZnO rod in the $X(YY)\vec{X}$, $X(ZY)\vec{X}$ and $X(ZZ)\vec{X}$ configurations, the results of polarized Raman indicated that these rods are crystallized and their growth direction is parallel to c -axis.

Keywords: ZnO; Co-doping; hydrothermal method; transmission electron microscopy; polarized Raman

1. Introduction

Zinc oxide is a wide band gap semiconductor (3.37 eV) with large exciton binding energy of 60 MeV at room temperature (Zhang *et al.* 2009). Doping various kinds of ions into ZnO is a useful method to improve their properties. Among these ions doped ZnO, the Co-doped ZnO has attracted much attention for its potential application in fabricating magnetic and electrical devices (Van *et al.* 2008, Patra *et al.* 2009). For example, Zhang *et al.* have reported that the Co-doped ZnO nanostructure can function as an electrical switch (2009). In order to meet the need of constituting devices, the fabrication of the Co-doped ZnO structures with different sizes and morphologies are becoming increasingly important.

Hydrothermal method is a stable and effective way to prepare homogeneously doped ZnO samples (Xie *et al.* 2008, Cheng *et al.* 2008). Better yet, this method can control the morphology and size of ZnO samples by changing the solvent. For example, Kanade *et al.* have reported that the size and morphology of ZnO particles change with the precursor solvent (Kanade *et al.* 2006), and Xie *et al.* have prepared ZnO crystals with different shapes and sizes by changing the proportion of water and alcohol in the mixed solvent (Xie *et al.* 2008).

In this work, Co-doped ZnO rods of nano-scale and micro-scale were successfully fabricated by the hydrothermal method. It has been observed that the size and doping content of the samples changed by using different solvents. The crystallinity and growth direction of the Co-doped ZnO nanorods have been examined by transmission electron microscopy (TEM). As for the Co-doped

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Table 1 The concentration of reactants used during the preparation

Sample	Solvent	Zinc acetate (mol/L)	Cobalt acetate (mol/L)	Sodium hydroxide (mol/L)	PEG-400 (mol/L)
Co-doped ZnO nanorods	Absolute alcohol	0.05	0.0025	0.8	0.4
Co-doped ZnO microrods	De-ionized water	0.05	0.0025	0.8	0

ZnO microrods with a diameter over 2 μm , it is difficult to detect them by TEM for the short penetration depth of electron. Consequently, we chose the polarized Raman measurement as an alternate to test the crystallinity of micro-sized ZnO structures.

2. Experimental section

2.1 Synthesis

The Co-doped ZnO rods were synthesized by a chemical method. The exact concentrations of the reactants are given in Table 1. The reaction process is as follows. The zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) and cobalt acetate ($\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$) were dissolved into a certain solvent, which is the de-ionized water or dehydrated ethanol. Then sodium hydroxide (NaOH) was dropped into the above two kinds of solutions with a constant stir. After that, the polyethylene glycol-400 (PEG-400) was added into the solution of ethanol, and did not be added into the solution of water. The deposition process was carried out at 160°C for 5 h in a Teflon-lined stainless autoclave tank. Finally, the two kinds of products were obtained from the aqueous solution and the ethanol solution, respectively, and then rinsed for several times by de-ionized water.

2.2 Characterizations

The morphology and component of the samples were characterized by field emission scanning electron microscopy (FE-SEM) (Zeiss, SUPRA-55) equipped with an energy-dispersive x-ray spectrometer (EDX) and an induced-coupled-plasma (ICP) (IRIS Intrepid II XSP). The crystal phase of the samples was characterized by x-ray diffraction technique using D8 discover with GADDS. The orientation of nano-crystals was analyzed by the high-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) (Jeol-2010, Japan).

Raman scattering and polarized Raman scattering were measured at room temperature by a Raman spectrometer (Jobin-Yvon, HR800) with an excitation wavelength of 514 nm. A small amount of the Co-doped ZnO microrods have been putted on a glass slice, and then be dispersed by dropping a droplet of ethanol. The position of the single rod under the optical microscope can be adjusted by rotating the slice. The polarization of the incident wave and scattered wave were selected with a half-wave plate and a polarizer, respectively.

3. Results and discussion

The insets of Fig. 1 show the FE-SEM images of Co-doped ZnO samples. The nanorods with a

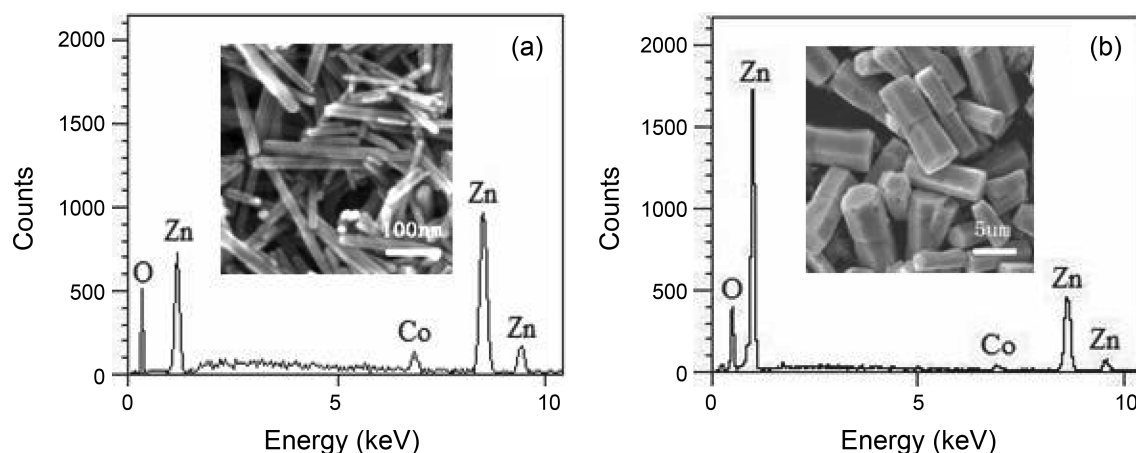


Fig. 1 (a) The EDX spectrum of the Co-doped ZnO nano-rods; (b) the EDX spectrum of the Co-doped ZnO micro-rods. The insets show the FESEM images of the corresponding samples

Table 2 The ICP measurement data and the calculated Co-doping content

Sample	Zn (mg/L)	Co (mg/L)	Co content
Co-doped ZnO nanorods	20.34	0.9478	5.17%
Co-doped ZnO microrods	19.90	0.3329	1.86%

diameter of 15-20 nm and a length of 150-200 nm were obtained in ethanol solution, and the microrods with a diameter of 2-5 μm and a length of 5-10 μm were obtained in aqueous solution.

The number of nucleation sites and the growth rate of crystals are the two main factors which determine the size of the samples which are prepared by hydrothermal method. The ZnO nanorods obtained in the ethanol solution mixed with a small amount of PEG-400 have larger crystal numbers and smaller particle size than those in aqueous solution. The reasons are as follows. Firstly, the two main reactants used to fabricate ZnO are NaOH and $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ in this work, and their solubility in water (109 and 30) are much higher than that in ethanol (17.3 and 0.042). The low solubility could cause an increase in the number of nucleation sites. Secondly, the Zn^{2+} in ZnO could bond with the oxygen of the hydroxyl group in ethanol. So the ethanol will adsorb on the surface of newly formed ZnO crystals and form an ethanol layer to stop the growth of ZnO crystals (Xie *et al.* 2009). Thirdly, the PEG-400 is both a disperser and a thickener, so the addition of it could not only increase the number of nucleation sites but also reduce the rate of grain growth.

The EDX results show that the Co contents in ZnO nanorods and microrods are $\sim 5\%$ and $\sim 2\%$, respectively (see insets of Fig. 1). In order to measure the Co contents more accurately, 2 mg Co-doped ZnO nanorods and microrods were placed separately into two beakers containing 100 ml de-ionized water and the ZnO samples were dissolved by adding a few drops of acetic acid. Then the solutions of Co-doped ZnO samples were test by ICP. The ICP measurement data of Zn, Co and the calculated Co-doping content in ZnO are shown in Table 2.

Although the proportion of the $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ are the same in the preparation process, the content of Co^{2+} in nanorods and microrods are different, which indicates that it is easier for the Co

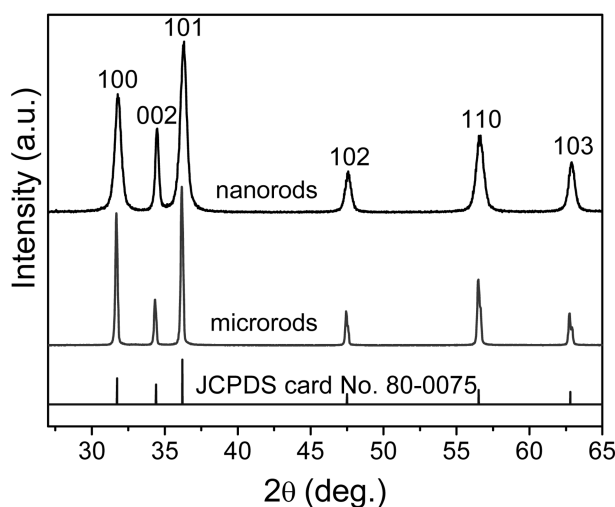


Fig. 2 The XRD patterns of Co-doped ZnO rods with different size

ion to be doped into the ZnO in ethanol solution than in aqueous solution.

XRD patterns of the as-prepared samples which were vertically normalized for clarity are shown in Fig. 2. The peaks of the Co-doped ZnO nanorods and microrods are in accordance with those of undoped ZnO (JCPDS card No. 80-0075), suggesting there is no second phase in wurtzite structure and the Cobalt in ZnO samples must have been in the form of ions. Since the radius of Co^{2+} (0.072nm) is only slightly less than that of the Zn^{2+} (0.074 nm) (Wang *et al.* 2007), the changes of peak positions are not obvious in the XRD pattern of Co-doped ZnO. By comparing the two kinds of Co-doped ZnO rods, it can be found that the nanorods show broader peaks than microrods, for their grain sizes are smaller.

Fig. 3 (a) and (c) show the TEM and HRTEM images of an individual Co-doped ZnO nanorod, which has been randomly chosen from the nanorods under the transmission electron microscope. The spacing of 0.26 nm between adjacent lattice planes corresponds to the distance of (0001) direction. The SAED pattern in Fig. 3(b) further proves the Co-doped ZnO nanorods have good crystallinity.

For ZnO has the wurtzite-type structure at ambient temperature and pressure condition (space group C_4^{6v}), six first-order modes can be expected, which are A_1 , E_1 , $2E_2$, and $2B_1$ (Arguello *et al.* 1969). The A_1 and E_1 modes are split into transverse (TO) and longitudinal optical (LO) phonons for their polarization. The two E_2 modes (E_2^{low} , E_2^{high}) are non-polar Raman active modes. The B_1 modes are silent modes for Raman.

Fig. 4 shows the Raman spectrum of the Co-doped ZnO microrods. The two intensive peaks at 98 cm^{-1} and 437 cm^{-1} are indicated to be E_2^{low} and E_2^{high} . The peak at 329 cm^{-1} is usually assigned to $E_2^{high} - E_2^{low}$ which is a second-order mode caused by multi-phonon processes. The peak at 377 cm^{-1} is known to be A_1 (TO). All of the peaks in Raman spectrum of Co-doped ZnO microrods didn't show much shift compared with the reported undoped ZnO crystal (Damen *et al.* 1966). Since the radius of Co^{2+} and Zn^{2+} are equivalent, the replacement of Zn^{2+} by Co^{2+} will certainly bring in little or no stress to the ZnO lattice. It has been reported that the LO peak at 580 cm^{-1} , which is related to oxygen defects, interstitial Zn and free carrier (Chen *et al.* 2005, Alaria *et al.* 2006), can

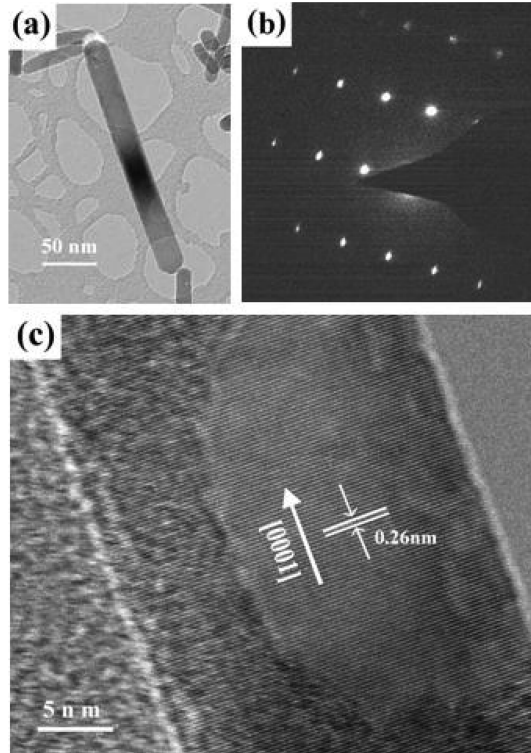


Fig. 3 (a) TEM image; (b) SEAD pattern; (c) HRTEM image of a Co-doped ZnO nanorod

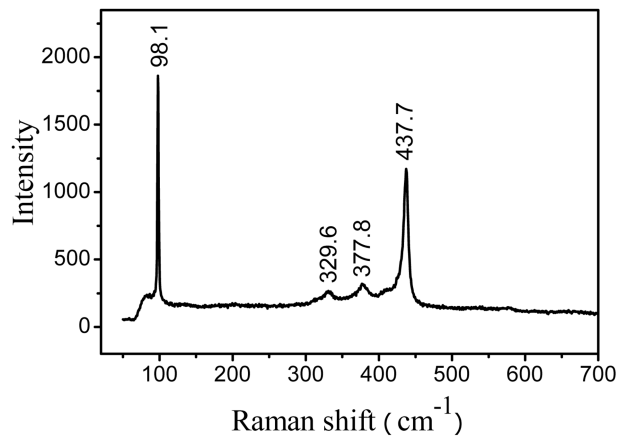


Fig. 4 The Raman spectrum of the Co-doped ZnO microrods sample

increase by doping Co^{2+} into ZnO (Phan *et al.* 2008, Duan *et al.* 2008). The absence of the LO peak in the Raman spectrum of the as-prepared Co-doped ZnO microrods indicates that the concentration of defects are low in the samples.

The inset of Fig. 5 shows the video image and polarization configuration of a Co-doped ZnO

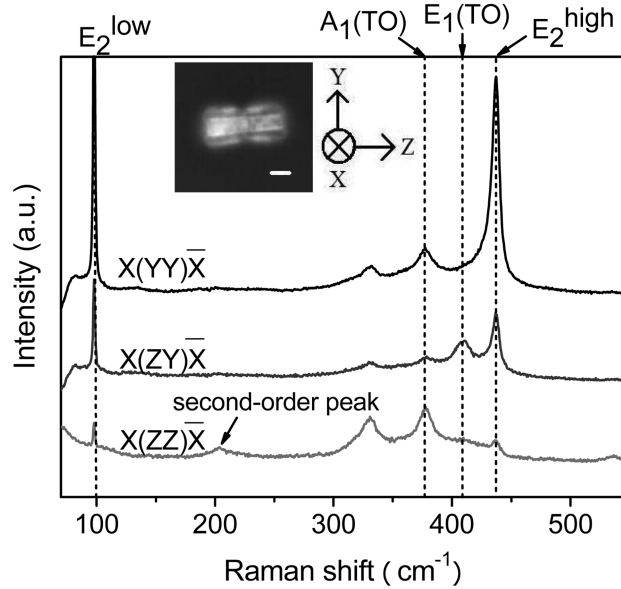


Fig. 5 Polarized Raman spectra in different polarization configurations; The inset shows the video image of an individual Co-doped ZnO rod. Scale bar=2 μm

microrod. The growth direction of the rod and the direction of incident wave are set as direction of Z axis and X axis, respectively. Four symbols are used to describe the set of polarization configuration. For example, $X(ZY)\vec{X}$ means that the incident wave propagates in $+X$ direction with the polarization direction paralleled to Z axis and the scattering wave propagates in $-X$ direction with the polarization direction paralleled to Y axis.

Fig. 5 shows the polarized Raman spectra in backscattering geometries. Firstly, the E_2 modes are the dominant peaks in $X(YY)\vec{X}$ configuration, whereas the intensity of E_2 modes are very weak in $X(ZZ)\vec{X}$ configuration. Secondly, the $A_1(\text{TO})$ mode is relatively strong in both $X(YY)\vec{X}$ and $X(ZZ)\vec{X}$ configuration, but is weaker in $X(ZY)\vec{X}$ configuration. Finally, the $E_1(\text{TO})$ mode could only be observed in $X(ZY)\vec{X}$ configuration and it didn't appear in other backscattering configurations. The anisotropic properties shown in polarized Raman spectra indicated that the Co-doped ZnO microrods have good crystallinity and the growth direction of them is perpendicular to (100) crystal plane.

Besides, a peak at 204 cm^{-1} appears in the $X(ZZ)\vec{X}$ configuration. Although the peak at 204 cm^{-1} is usually assigned to be a second-order mode of E_2^{low} , we attribute it to be 2TA . For the peak at 204 cm^{-1} can only be observed in the $X(ZZ)\vec{X}$ configuration in our work, which means it is of A_1 symmetry. The enhancement of this peak may be caused by the long range order of Co ion along the c -axis.

4. Conclusions

In summary, the Co-doped ZnO rods with nano-size and micro-size were both obtained through a

chemical route. Different solvents were used during the preparation, which cause the different sizes of the final products. The Co^{2+} is apt to go into the ZnO lattice when ethanol is used as solvent. The results of transmission electron microscopy and polarized Raman respectively proved that the Co-doped ZnO nanorods and Co-doped ZnO microrods are both with good crystallinity.

Acknowledgements

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