doi:10.1246/cl.2011.390

Synthesis and Optical Properties of Co-doped ZnO Nanoparticles

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Pure and Co-doped ZnO nanoparticles were synthesized by a sol–gel method. The structure, morphology, and properties of as-prepared samples have been studied using X-ray diffraction (XRD), transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS), and ultraviolet–visible absorption spectroscopy (UV–vis) as well as by photoluminescence (PL) spectrometry. The results showed that the diameter of the well-dispersed Co-doped ZnO nanoparticles is about 5 nm and that dopant Co^{2+} ions substitute Zn^{2+} ions sites in ZnO nanocrystals without forming any secondary phase. The optical measurements show that the Co doping can effectively tune energy band structure and enrich surface states in both UV and VL regions, which lead to novel PL properties of ZnO nanoparticles. Compared to the undoped sample, a new emission caused by transitions between localized Co^{2+} d levels appears at 624 nm.

Owing to unique properties such as wide band gap (3.37 eV), large exciton binding energy (60 meV), and superior conducting properties,[1] wurtzite-structured ZnO has become one of the most promising materials for the fabrication of high-technology applications such as photonic crystals, light-emitting diodes, sensors, and electro- and photoluminescent materials.[2] It has been theoretically predicted that the addition of impurities into a wide gap semiconductor can often induce dramatic changes in the properties.[3] In recent years, several types of metal ions have been doped into the ZnO crystal lattice. For example, group IIIA elements (such as Al, Ga, and In) have been used to substitute Zn sites to induce n-type semiconduction.[4] Group IA elements (such as Li, Na, and K) can improve the optical properties of ZnO by occupying interstitial sites due to their small ionic radii.[5] In addition, ZnO is doped with Sn, Sc, and Y, in order to improve its transparent conducting oxides (TCO) properties.[6] Doping of ZnO with magnetic ions such as Fe, Co, and Ni introduces magnetic properties forming dilute magnetic semiconductors (DMSs).[7] Therefore, selection of proper doping elements in ZnO has become an important route for enhancing and controlling electrical, optical, and magnetic performance of nanomaterials. Generally, Co is one of the most effective dopants to tune both optical and magnetic properties due to its abundant electronic states as well as its very small influence on ZnO lattice structure. Up to now, many studies have been done on the magnetic properties of thin Co-doped ZnO films and nanoparticles. However, the influences of Co doping in ZnO nanoparticles on optical characteristics are seldom investigated, whereas these are extremely important for practical application of ZnO nanomaterials in light-emitting diodes (LED).

In this paper, we successfully synthesized Co-doped ZnO nanoparticles using a simple aqueous solution with controlled Co content. This method may be used for preparation of many new device materials in microscale electronics and photonics such as novel memory and optical devices, and it will be applied in biological detecting and treatment. As the doped Co concentration is far below the solubility limit of Co in ZnO matrix,[8] it can effectively diminish the possibility of secondary impurity phases. On this basis, optic properties of $Zn_{1-x}Co_xO$ nanoparticles were carefully investigated with different Co-doping concentrations ($x = 0$–0.04).

Synthesis of colloidal $Zn_{1-x}Co_xO$ precursor was achieved by addition of LiOH base to an original mixture solution of zinc acetate ($ZnAc_2$) and cobalt acetate ($CoAc_2$) in ethanol, forming colloidal $ZnO{:}Co^{2+}$ through hydrolysis and condensation. This method is similar to a process reported by Spanhel[9] for undoped ZnO quantum dots. Co doping concentration in the range of 1–4% was achieved in this work. To eliminate undesirable byproducts such as acetates, the colloid was carefully washed with deionized water and ethanol. In the end a highly dense purple-blue transparent colloid was obtained. By drying the colloid in air we could also obtain a powder of $Zn_{1-x}Co_xO$ ($x = 0$, 0.01, 0.02, and 0.04) nanoparticles.

The phase and composition of the products were characterized by X-ray diffraction (XRD) using a Rigaku D/max 2500 diffractometer at a voltage of 40 kV and a current of 200 mA with Cu Kα radiation ($\lambda = 1.5406$ Å), employing a scanning rate $0.02°\,s^{-1}$ in the 2θ ranging from 20 to 70°. High-resolution transmission electron microscopy (HRTEM) images were obtained by using a JEM 2100F field-emission transmission electron microscope operated at an accelerating voltage of 200 kV. The Co content was determined using energy-dispersive X-ray spectroscopy (EDS). Room-temperature absorption spectra were recorded using a Lambda 900 UV–vis–NIR spectrophotometer. The photoluminescence (PL) measurements were performed on a Hitachi F-4500 fluorometer with a Xe lamp as the excitation light source at room temperature. The excitation wavelength was 330 nm.

The crystal structure of synthesized samples has been investigated using XRD. Figure 1 shows XRD patterns of pure and Co-doped ZnO nanoparticles. All diffraction peaks from undoped and doped ZnO samples are indexed to hexagonal wurtzite structure (JCPDS No. 36-1451), which revealed that Co^{2+} ions systematically substitute Zn^{2+} ions in the ZnO nanocrystal without changing the wurtzite structure. The diffraction intensities of doped sample are weaker compare to undoped ZnO nanorods, which illustrate that Co doping can slightly impede the ZnO crystallinity. In addition, no cobalt metal, oxides, or any other zinc cobalt phase is detected in diffraction patterns which illustrate that the obtained samples are highly pure single phase.

In order to be confident that there are no small precipitates of impurity phase and Co metals, HRTEM has been used. The

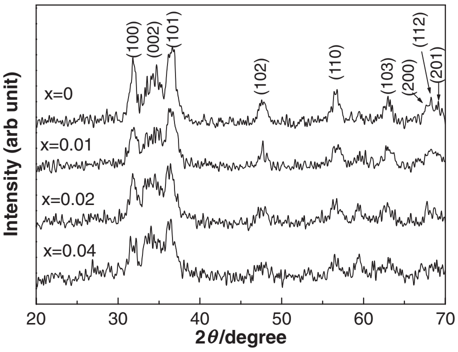

Figure 1. XRD patterns of pure and Co-doped ZnO nanoparticles.

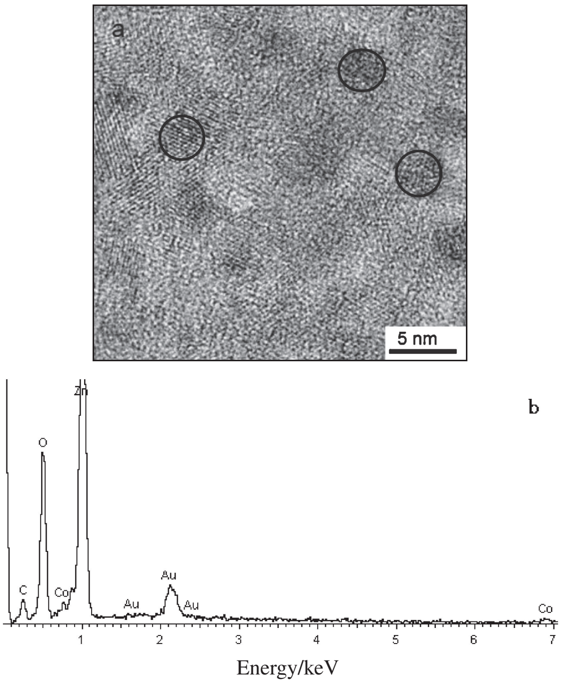

Figure 2. (a) HRTEM image and (b) the energy-dispersion spectroscopy analyze of $Zn_{0.96}Co_{0.04}O$ samples.

HRTEM image of $Zn_{0.96}Co_{0.04}O$, shown in Figure 2a, indicates that the particles are of ca. 5 nm, and that the $Zn_{0.96}Co_{0.04}O$ nanoparticles exhibit a very uniform microstructure. This strongly suggests that Co atoms were incorporated uniformly into the entire ZnO material and that no segregated metals of impurity phase appeared. Figure 2b shows the EDS spectra from Co-doped ZnO nanoparticles. The sample has an oxygen peak at 0.53 keV and Zn signals at 1.03 keV. The Co signals at 0.75 and 6.89 keV were observed in the Co-doped ZnO nanoparticles. Quantitative analysis showed concentrations of Co of about 4.5%, which was slightly larger than that of the corresponding calculated concentration in preparations for 4.0%. The Au and C signals originate from the Au spraying and conducting resin during measurements, respectively.

Substitution of Co cations in tetrahedral sites of the wurtzite structure was further confirmed by UV–vis optical spectroscopy. The room-temperature spectra of the $Zn_{1-x}Co_xO$ nanoparticles are reported in Figure 3a and compared to the spectrum recorded for the ZnO reference sample. From Figure 3a, the band edges are shifted to higher energy in the Co-doped ZnO samples, except that of the $Zn_{0.99}Co_{0.01}O$ samples. Compared to the undoped sample, the band edge of doped ZnO nanoparticles became narrow, and then wider. The increase in the band edge is a clear indication of the incorporation of Co inside the ZnO lattice,[10] which is consistent with the calculated values recorded in Figure 3b. When the doped Co^{2+} enters into the ZnO crystal structure, the localized band edge states form at the doped sites with an increase of E_g due to the crystal lattice confinement effect.

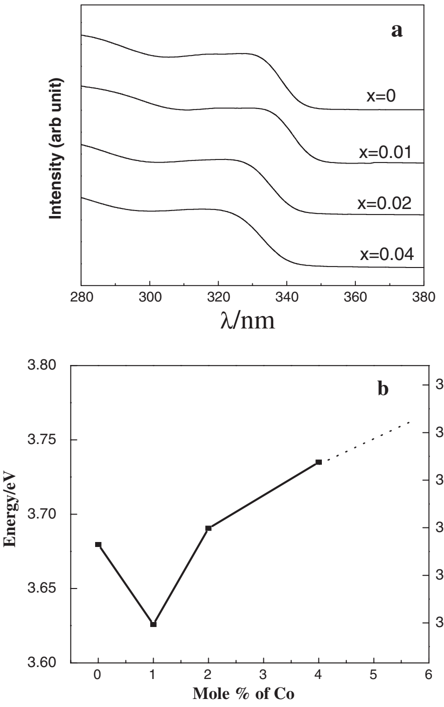

Figure 3. (a) The UV absorption curves of ZnO and $Zn_{1-x}Co_xO$; (b) Variation of band gap with the percentage of Co doping in nanoparticles.

The optical properties of the as-synthesized samples have been investigated by PL spectrum at room temperature. Figure 4 shows the PL spectra of pure and Co-doped ZnO nanoparticles. In Figure 4, there are two obvious PL regions from both pure and Co-doped ZnO nanoparticles. One is a strong spontaneous emission peak in the UV region, which originates from a near-band-edge (NBE) transition of wide band gap of ZnO,[6b,11] namely, the recombination of free excitions through an exciton–exciton process, while the VL luminescence band in the range 400–650 nm is related to defects and oxygen vacancies in nanomaterials.[12] By comparison, it can be found that a new emission appears at 624 nm, and with the increase of Co concentration, the intensity of the peaks gradually increased. It most likely originates from the coordinative, unsaturated Zn sites in the ZnO nanoparticles, transitions between localized Co^{2+} d levels or the formation of band tailing in the band gap, which is often induced by the introduction of impurities into the semiconductor.[2,13] In addition, there are three interesting changes in the PL spectra from undoped to Co-doped ZnO

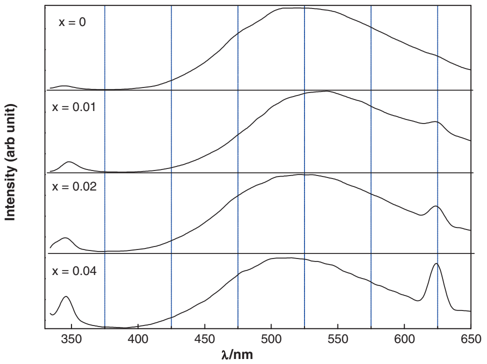

Figure 4. PL spectrum of Co-doped samples measured at room temperature.

samples: (i) the emission intensity of doped ZnO nanoparticles increases in the UV region compared to pure ZnO, which illustrates that Co doping can effectively improve separation of photoinduced carriers in NBE; (ii) the position of emission peaks shifts toward shorter wavelength in the VL region, except the $Zn_{0.99}Co_{0.01}O$ sample. This well agrees with the UV–visible spectra, showing that the Co-doped ZnO nanoparticles have high optical properties. (iii) with the increase of the concentration of dopant, the intensity of green emission peaks at 530 nm became a little weaker. This might be ascribed to the oxygen vacancy and the transition of a photogenerated electron from a dark level below the conduction band to a deeply trapped hole.[14]

In summary, Co-doped ZnO nanoparticles have been successfully synthesized by a simple aqueous solution route. The as-prepared products are in wurtzite structure. Photoluminescence spectra demonstrated that Co-doped ZnO nanoparticles exhibit a near band edge UV emission peak centered at about 348 nm and a green emission peak centered at about 530 nm. Compared to the undoped sample, a new emission caused by transitions between localized Co^{2+} d levels appear at 624 nm.

This work was financially supported by the Overseas Outstanding Scholar Foundation of Chinese Academy of Sciences (Grant Nos. 2005-1-3 and 2005-2-1), Shanghai Municipal Natural Science Foundation (Grant No. 10ZR1412200), the Specialized Research Fund for Outstanding Young Teachers in Shanghai Higher Education Institutions (Grant No. egd08013), and the Innovation Program of the Shanghai Municipal Education Commission (Grant No. 10YZ200).

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