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Effects of Cr-doping on the optical and magnetic properties in ZnO nanoparticles prepared by sol–gel method

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ABSTRACT

The undoped ZnO nanoparticles and the Cr-doped ZnO nanoparticles were successfully synthesized by the sol-gel method. The structure, the optical characteristics and the magnetic properties of the produced samples were studied. The results indicated that Cr ions substituted for Zn ions successfully and the Cr-doping restrained the growth of the crystal lattice. The Cr ions exhibited +3 valence state other than +2 valence state. The dopant concentration was about 3 atm% in the Cr-doped ZnO nanoparticles, which was consistent with the design of our experiment. Compared with the photoluminescence (PL) spectrum of the ZnO nanoparticles, the peak position of ultraviolet (UV) emission of the Cr-doped ZnO nanoparticles exhibited blue shift, and the deep level emission band was sharply suppressed. Moreover, the Cr-doped ZnO nanoparticles had good ferromagnetic property at room temperature.

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1. Introduction

Diluted magnetic semiconductors (DMSs), with Curie temperature (Tc) at or above room temperature, have potential application in the spintronic devices such as, magnetic random access memories, optical isolators and quantum computers, etc. [1,2]. The term DMS refers to the fact that some fractions of the atoms in a nonmagnetic host such as ZnO, TiO₂, SnO₂ and In₂O₃, are replaced by transition metal (TM) ions [3–6]. Among the nonmagnetic matrixes, since ZnO has wide band gap (3.37 eV) and large exciton binding energy (60 meV), ZnO-based DMSs have been extensively investigated in recent years [7–9]. For example, Dietl et al. predicted that Mn-doped ZnO was ferromagnetic at room temperature [10]. Later, Sato et al. further predicted that ZnO doped with Cr, V, Fe, Ni and Co could be ferromagnetic [11].

Among dopant elements, Cr dopant is particularly interesting and it has attracted lots of attention [12,13]. One of the reason is that radius parameter of Cr^{3+} is closer to that of Zn^{2+} , which means that Cr^{3+} can easily penetrate into the ZnO crystal lattice or substitute for the position of Zn^{2+} in crystal ZnO [14]. In particular, unlike many other metals, Cr itself is antiferromagnetic and it will not induce an extrinsic ferromagnetism even if Cr clustering occurs. Venkatesan et al. and Jin et al. did not find any indication of ferromagnetism for Cr-doped ZnO film at low temperature even down to 3 K [15,16]. However, based on the experimental and the theoretical study, Elanchezhiyan et al. indicated that Cr-doped ZnO films were ferromagnetic [17,18]. Therefore, the magnetic properties of Cr-doped ZnO are far from being clear, so more detailed and probing investigations are necessary to reveal the nature of this material.

Since the way that Cr^{3+} enters the ZnO lattice as a result of substitution or interval determines the occurrence of the intrinsic defects or the extrinsic defects [13], the problem of how Cr^{3+} enters the ZnO lattice is rather important. It is worth to notice that, for the TM-doped ZnO semiconductors, many groups validated that TM ions had substituted successfully for Zn^{2+} in crystal only through the analysis of X-ray diffraction (XRD) [19]. Considering the limit of XRD itself, the result of XRD alone is obviously not enough to determine the position of Cr^{3+} in ZnO lattice. In addition, it is possible that the secondary phases exist in the materials, but its concentration is below the detection limit and cannot be detected by XRD. The secondary phase is a concern in any diluted magnetic system as a source of spurious magnetic signal. It is necessary to adopt other instruments as assistant methods to verify the behavior of Cr^{3+} in the ZnO crystal lattice.

In this present work, the undoped and the Cr-doped ZnO nanoparticles were synthesized by sol-gel method. We tried to use several measuring instruments, such as XRD, high-resolution transmission electron microscopy (HRTEM), energy dispersive

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Fig. 1. XRD patterns of the pure ZnO (a) and the Cr-doped ZnO (b).

spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), to verify that Cr^{3+} does substitute for Zn^{2+} in the crystal lattice. Furthermore, we studied the effects of Cr-doping on optical and magnetic properties in ZnO nanoparticles.

2. Experimental details

All the chemical reagents in our experiment were of analytical grade purity. The initial materials included zinc nitrate $[Zn(NO_3)_2.6H_2O]$, chromium nitrate $[Cr(NO_3)_3.9H_2O]$ and citrate acid ($C_6H_8O_7.H_2O$). Zinc nitrate and the appropriate amounts of chromium nitrate (Zn:Cr = 0.97:0.03, in mol) were dissolved into the citrate acid to form the sol with stirring. Then, the mixture was polymerized to form

the gel at 80 °C. When the swelled gel was pyrolyzed at 130 °C, the amorphous composite precursor was obtained. The precursor was further ground into powder in an agate mortar. Finally, the powder of the precursor was sintered at 400 °C for 10 h in the tube furnace with the air atmosphere as the carrying gas.

The structure characterization of the Cr-doped ZnO nanoparticles was performed by XRD on D/max-2500 copper rotating-anode X-ray diffractometer with Cu K α radiation (40 kV, 200 mA). The size distribution and the interplanar distance were investigated by the transmission electron microscope (TEM) (200 keV, JEM-2100HR, Japan). The magnetic hysteresis loops of the Cr-doped ZnO were measured by a Lake Shore 7407 vibrating sample magnetometer (VSM). The valence state of the Cr element was analyzed by X-ray photoelectron spectroscopy (XPS) (VG ESCALAB Mark II). The PL measurement was performed on an HR800 Labram Infinity Spectrophotometer, which was excited by a continuous He–Cd laser at the wavelength of 325 nm and the output power of 50 mW.

3. Results and discussion

Fig. 1 shows the XRD patterns of the undoped ZnO (Fig. 1a) and the Cr-doped ZnO (Fig. 1b). Both diffraction peaks can be indexed to the wurtzite hexagonal ZnO (space group *P*63*mc*) without any other impure phases. As for ZnO, the cell constant is estimated to be a = 0.3256 nm, c = 0.5218 nm, and the volume is 0.04791 nm³ (Fig. 1a). However, as for the Cr-doped ZnO, the cell constant is estimated to be a = 0.3254 nm, c = 0.5216 nm, and the volume is 0.04782 nm³ (Fig. 1b), which is a little smaller than that of the undoped ZnO. The result can be ascribed to the substitution of the Cr ions with a small ionic radius of 0.063 nm for Zn (0.074 nm) sites [20].

From the XRD spectrum, we also can observe that the full width at half-maximum (FWHM) of the diffraction peak of the Cr-doped ZnO is much wider than that of the undoped ZnO. The average grain size estimated from the FWHM of three main peaks by Debye–Scherrer formula is 26.2 and 11.1 nm, respectively. Generally speaking, the growth of the ZnO grains is determined by the move-



Fig. 2. TEM and HRTEM images of the pure ZnO nanoparticles (a), (b) and the Cr-doped ZnO nanoparticles (c), (d); the inset figure is the EDS spectrum.



Fig. 3. XPS spectrum of Cr-doped ZnO nanoparticles.

ment and the diffusion of Zn^{2+} or Zn_i^x . However, in the Cr-doped ZnO, Cr maybe exist at the grain boundaries, which can enhance the energy barrier of the movement and the diffusion of Zn^{2+} or Zn_i^x to suppress the diffusion of Zn^{2+} or Zn_i^x , therefore, restrain the growth of the ZnO grains [21].

The morphology and structure characterizations were investigated by TEM and HRTEM. The images of the pure ZnO samples (a), (b) and the Cr-doped ZnO samples (c), (d) are shown in Fig. 2. It can be seen that both samples are spherical shape and both of them show the narrow size distribution. The average particle size is about 26 nm for Fig. 2(a) and about 11 nm for Fig. 2(c), which is in agreement with the XRD result. In addition, it can be clearly observed from the HRTEM figures that the interplanar distance is 0.26 nm for both the pure ZnO and the Cr-doped ZnO samples, which is corresponding to the (002) planes of the wurtzite ZnO. The inset of Fig. 2(d) is the EDS spectrum of a single Cr-doped ZnO nanoparticle. Although we cannot exactly determine the Cr concentration by this method, it does show the existence of the Cr ion in the Cr-doped ZnO. We would like to point out that the similar values of the Cr concentration are observed at a dozen of Cr-doped ZnO nanoparticles, which indicates that the variation of Cr content is rather small and the Cr dopant is uniform throughout the specimen. These results further testified that Cr ions were substitutionally incorporated into the crystal lattice of ZnO.

The Cr $2p_{3/2}$ and Cr $2p_{1/2}$ XPS spectral regions of the Cr-doped ZnO nanoparticle are shown in Fig. 3. Based on the Gauss fitting, the Cr $2p_{3/2}$ peak position is at 576.6 eV in the Cr-doped ZnO nanoparticles. It is clearly different from 574.2 eV of Cr metal and 576.0 eV of Cr²⁺. But it is quite close to the peak position of Cr $2p_{3/2}$ (576.7 eV) in Cr₂O₃ [16]. It suggests that Cr dopants are actually incorporated into the ZnO lattice as Cr³⁺ ions instead of Cr²⁺ ions.

Fig. 4 shows the PL spectra of the pure ZnO and the Cr-doped ZnO nanoparticles excited by 325 nm at room temperature. The inset of Fig. 4(b) is the PL spectra by using logarithmic coordinates. The PL spectrum of the pure ZnO nanoparticles consists of a dominant UV peak at 401 nm in wavelength and a very broad deep level emission band in the range of 470-700 nm. The UV emission band is related to a near band-edge transition of ZnO [22-24], namely, the recombination of the free excitons. In comparison with the pure ZnO, the UV emission peak position of the Cr-doped ZnO nanoparticle exhibits blue shift, and the deep level emission band is sharply suppressed, which indicates that the existence of Cr dopants can enhance the excitonic recombination radiation. The results are well coincided with the results in the literature [9]. As for the Cr-doped ZnO nanoparticles, more electrons caused by chromium dopants will take up the energy levels located at the bottom of conduction band. When they are excited by the laser of 325 nm, the excitons will take up higher energy levels at the bottom of the conduction band. The radioactive recombination of these excitons will lead to blue shift and the broadening of the UV emission peak [25]. In addition, the lattice strain induced by the lattice distance will lead to blue shift in the band gap. But it may not play a major role in the determination of the band gap as the small deformation of the lattice distances. So, the blue shift of the UV emission also testifies the fact that at least a part of Cr ions are incorporated into the lattice sites. As far as the deep level emission is concerned, it has recently



Fig. 4. PL spectra of the pure ZnO (a) and Cr-doped ZnO (b).



Fig. 5. The magnetic hysteresis (M–H) curve of the pure ZnO (a) and the Cr-doped ZnO (b).

been attributed to at least two different defect origins, the oxygen vacancy (V_0) and the zinc vacancy (V_{Zn}) with different optical characteristics [26–28]. In our case, the Cr-doping sharply suppressed this part emission. We think maybe part of Cr dopants also take the place of V_{Zn} and decrease the quantity of the defect.

As is known to all, the pure ZnO nanoparticles are paramagnetic materials, which are also confirmed by our experiments. However, the Cr-doped ZnO nanoparticles exhibit obvious hysteresis loop at room temperature (M-H curve, shown in Fig. 5), which demonstrates that the Cr-doped ZnO nanowires have good ferromagnetic property at room temperature. The saturation magnetization (Ms) of the Cr-doped ZnO nanoparticles is estimated to be about 2.2×10^{-3} emu g⁻¹, and the remnant magnetization (Mr) and the coercive field (Hc) are 4.1×10^{-4} emu g⁻¹ and 430 Oe, respectively. According to the references, two key factors probably lead to the appearance of ferromagnetism in TM-doped ZnO nanocrystals: one is the increase of the number of defects and oxygen vacancies [29], for example, Xing et al. have reported that the ferromagnetism is stronger in Cu-doped ZnO nanowires with higher oxygen deficiency [6]; the other is the exchange interactions between TM ions and O ions spin moments, for instance, Chu et al. predicted that most of the magnetic moment is induced by Cr 3d and O 2p spin moments through the theoretical calculations [19]. But according to the PL result, we have already known that the concentration of the defects decreases because of the Cr-doping. So in our case, the latter one, exchange interactions between Cr 3d and O 2p spin moments, should be the main reason for the ferromagnetic behavior in the Cr-doped ZnO nanoparticles. These are well in agreement with the hypothesis exhibited in the PL experiments and the theoretical calculations in the literature [30].

4. Conclusions

In this paper, the undoped and the Cr-doped ZnO nanoparticles were synthesized by sol-gel method. Different measuring equipments were used to characterize the structure of both nanoparticles. And we verified successfully that the Cr ions had taken the place of the Zn ions with +3 valence state in ZnO lattice, and the Cr-doping could restrain the growth of the crystal lattice. We also found that due to the disappearance of the deep level emission band in PL spectrum, the Cr-doping could improve the optical properties. It could also keep the sample in good ferromagnetic property at room temperature because of the exchange interactions between Cr 3d and O 2p spin moments. These results of our investigation provided an effective way to enhance both optical and magnetic properties of the ZnO nanoparticles, which will play an important role in prompting its practical application in the future.

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