Structural and optical properties of cobalt doped ZnO nanocrystals

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\textbf{Abstract}

Zn\textsubscript{1-x}Co\textsubscript{x}O nanocrystals with nominal Co doping concentrations of \(x = 0–0.1\) were synthesized through a simple solution route followed by a calcining process. The doping effects on the structural, morphological and optical properties were investigated by means of X-ray diffraction, scanning electron microscopy, transmission electron microscopy, Raman, absorption and luminescence spectroscopy. The results indicated that a small amount of Co ions were incorporated into ZnO lattice structure, whereas the secondary phase of Co\textsubscript{3}O\textsubscript{4} was segregated and precipitated at high Co doping concentrations, the solid solubility of Co ions in ZnO nanocrystals could be lower than 0.05. The spectra related to transitions within the tetrahedral Co\textsuperscript{2+} ions in the ZnO host crystal were observed in absorption and luminescence spectra.

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1. Introduction

Zinc oxide (ZnO) with a direct wide band gap (3.37 eV) and a large exciton binding energy (60 meV) is considered to be one of the most important semiconductor materials for applications in electronics, optoelectronics, spin electronics and sensors devices \cite{x1–4}. Intentional introduction of impurities or dopants into a semiconductor is an effective approach to change its electronic structure and then
modify the electronic, optical and magnetic properties of the material. For example, the incorporation of Al into ZnO can lead to an increase in the carrier concentration [5]. Mg dopants can widen the band-gap of ZnO thin films [6]. Numerous theoretical analysis and experimental researches reveal that 3d transition metal (TM) ions substitutionally doped into ZnO lattice can induce ferromagnetic order [7–9] or improve photocatalytic activity [10,11]. To date, great efforts have been devoted to the investigation of TM doped ZnO nanostructures due to their wide applications.

However, it is pointed out that doped ions in ZnO nanostructures tend to locate near the surface for “self-purification” [12] and the physical or chemical properties of impurity-doped ZnO nanostructures depend on the surface structure and the chemical environment around dopant. Schwartz et al. have found that intermediate Co$^{2+}$ ligand field and substitutional Co$^{2+}$:ZnO ligand field exhibit different absorption characteristics [13]. Bohle et al. have reported that the external doping and internal doping can result in various degree of fluorescence quenching [14]. In addition, the mechanism of the ferromagnetism of Co-doped ZnO is still under debate due to segregation of secondary phase. So it is critical to obtain the information of the state of doping ions in ZnO. The segregation of second phase is difficult to detect by only one conventional means. More detailed works are essential to understand the nature of impurity states. Photoluminescence (PL) spectra measurement is a technique for the investigation of electronic excitation and has been widely used for exploring the energy levels in ZnO. The detailed studies of the impurity-related PL are important for the understanding of the nature of dopant states in nanocrystals and new functionalities of impurity-doped nanocrystals.

In this paper, Zn$_{1-x}$Co$_x$O nanocrystals with nominal Co doping concentrations of $x = 0$–0.1 were synthesized through a simple solution route followed by a calcining process. The structural, morphological and optical properties of Zn$_{1-x}$Co$_x$O nanocrystals were investigated. X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Raman techniques were used to characterize the crystal structure, particle size and morphology of the samples. The absorption and PL spectra were performed to probe the electronic structure of Co ions in the ZnO host.

2. Experimental

2.1. Synthesis of Zn$_{1-x}$Co$_x$O nanocrystals

Zinc acetate dihydrate (Zn(Ac)$_2$·2H$_2$O, Tianjin Kewei Ltd.), cobalt acetate tetrahydrate (Co(Ac)$_2$·4H$_2$O, Tianjin Kewei Ltd.), oxalic acid dihydrate (H$_2$C$_2$O$_4$·2H$_2$O, Tianjin Jiangtian Chemical Ltd.) and absolute ethanol (Tianjin Kewei Ltd.) of analytical purity were purchased and used as received.

The detailed experimental procedures for Zn$_{1-x}$Co$_x$O ($x = 0, 0.01, 0.03, 0.05, 0.07, 0.1$) nanocrystals were as follows [15]: 1 mmol Zn( Ac)$_2$·2H$_2$O and $y$ mmol ( $y = 0, 0.001, 0.003, 0.005, 0.007, 0.01$) Co( Ac)$_2$·4H$_2$O were dissolved in 100 mL de-ionized water. 1.5 mmol H$_2$C$_2$O$_4$·2H$_2$O dissolved in 100 mL de-ionized water was added dropwise into the above solution under magnetic stirring. After stirring at room temperature for 12 h, the Co and Zn oxalate were formed and separated from the solution by filtration, washed two times with de-ionized water and three times with absolute ethanol, then dried in air at 90 °C for 10 min to remove residual solvent. The obtained nanocrystalline powders were then calcined in air at 450 °C for 1 h.

2.2. Characterization

The crystal structure of Zn$_{1-x}$Co$_x$O nanocrystals was analyzed using a Rigaku D/Max-2200 X-ray diffractometer with a Cu-Kα radiation ($\lambda = 1.5406$ Å). Raman spectra were acquired from LabRam micro-Raman spectrometer with the wavelength of 533 nm laser excitation at room temperature. The morphologies of Zn$_{1-x}$Co$_x$O nanocrystals were characterized by SEM (JEOL/JSM 6700F NT) and TEM (JEOL EM-2010F). UV–Vis absorption spectra were recorded on a Hitachi 4100 UV–Vis spectrophotometer. PL spectra were monitored by a spectrometer (FluoroLog 3, Horiba Jobin Yvon) using 450 W Xe lamp.
3. Results and discussion

3.1. Structural and morphological analysis

Fig. 1 shows the XRD patterns of Zn$_{1-x}$Co$_x$O nanocrystals with different Co doping concentrations. It is found that all the samples possess a typical hexagonal wurtzite structure by comparison with the data from JCPDS standard cards (PDF#80-0075). For Zn$_{1-x}$Co$_x$O nanocrystals with high doping concentrations, weak diffraction peaks of Co$_3$O$_4$ can be detected, as shown in the insert of Fig. 1, indicating that the Co ions can be incorporated into the ZnO crystal structure to form a solid solution at a low doping concentration. Impurity phases such as Co$_3$O$_4$ can be segregated in the surface or grain boundary of ZnO at high doping concentrations under annealing condition [16]. As Co ions were incorporated into ZnO lattice, the crystal lattice distortion can be induced. The crystal lattice distortion degree can be determined by the following equation [17]:

$$ R = \frac{(2a\sqrt{2/3})}{c} $$

where $a$ and $c$ are lattice constants and can be calculated from the XRD patterns. The crystal lattice distortion degrees of samples with different Co doping concentrations are listed in Table 1. Table 1 reveals that the crystal lattice distortion degree firstly increases, then reaches saturation at Co concentration $x = 0.03$, and then decreases with increasing Co concentration, indicating that the solid solution limit of Co ions in ZnO nanocrystals could be lower than 0.05. A small amount of secondary phases with disoriented distribution may be insufficient to form adequate sharp peaks to be detected by XRD patterns because XRD is only sensitive to long-range crystalline order, so that the segregated impurities cannot be detected in XRD patterns of Zn$_{0.95}$Co$_{0.05}$O nanocrystals probably due to the limited resolution of our XRD instrument as well as amorphous structure of the impurities. In addition, the XRD peak intensity is reduced obviously and the full width at half maximum (FWHM) increases with the increase of Co concentration, indicating that the crystalline quality of the nanocrystals is very sensitive to the addition of Co. The average crystallite size of the samples with different Co concentrations presented in Table 1 has been evaluated from the FWHM by using Scherrer’s formula [18]. It decreases from $\sim$23 nm to $\sim$15 nm as Co concentration changes from 0 to 0.1.

Fig. 2 shows the SEM images of Zn$_{1-x}$Co$_x$O nanocrystals with different Co concentrations. An abundance of nearly spherical particles are recognized for all samples. The average diameter of particles decreases with increasing Co concentration, in agreement with the obtained XRD results. Since the ionic radius of Co$^{2+}$ is a little smaller than that of Zn$^{2+}$, the lattice structure can be distorted by Co.

![Fig. 1. XRD patterns of Zn$_{1-x}$Co$_x$O nanocrystals with different Co doping concentrations; the inset shows enlarged view of XRD patterns for $x = 0.07$ and $x = 0.1$ (the diamond denotes impure phase).](image-url)
substitution. Also, segregation of impurities on the surface or grain boundary can suppress the growth of crystalline grain for $\text{Zn}_{1-x}\text{Co}_x\text{O}$ nanocrystals with high doping concentrations [19].

The morphology and phase structure of the samples were further studied by TEM. The typical TEM images of $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$ nanocrystals were presented in Fig. 3(a) and (b). Fig. 3(a) shows the low magnification TEM micrograph. The corresponding particle size distribution histogram of $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$ nanoparticles is given in Fig. 3(c), the average particle diameters were found to be approximately 15–20 nm, which is consistent with XRD results. A HRTEM image recorded from a particle is shown in Fig. 3(b). A nice crystallinity and clear lattice fringes can be observed, indicating that the nanocrystal is single crystalline. The lattice spacing between two adjacent lattice fringes is 2.8 Å, which corresponds to the interplanar spacing of (100) plane of hexagonal wurtzite ZnO.

### Table 1
Nominal Co concentrations, the lattice constants calculated according to the XRD data and distortion degree calculated according to the lattice constants.

<table>
<thead>
<tr>
<th>Doping concentration</th>
<th>0</th>
<th>0.01</th>
<th>0.03</th>
<th>0.05</th>
<th>0.07</th>
<th>0.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ (nm)</td>
<td>0.32551</td>
<td>0.32557</td>
<td>0.32567</td>
<td>0.32556</td>
<td>0.32548</td>
<td>0.32564</td>
</tr>
<tr>
<td>$c$ (nm)</td>
<td>0.52143</td>
<td>0.52137</td>
<td>0.52134</td>
<td>0.52134</td>
<td>0.52131</td>
<td>0.52160</td>
</tr>
<tr>
<td>Distortion degree</td>
<td>1.0194</td>
<td>1.0197</td>
<td>1.0200</td>
<td>1.0197</td>
<td>1.0195</td>
<td>1.0194</td>
</tr>
<tr>
<td>Particle size (nm)</td>
<td>22.8</td>
<td>19.9</td>
<td>18.0</td>
<td>16.3</td>
<td>15.9</td>
<td>14.9</td>
</tr>
</tbody>
</table>

Fig. 2. SEM images of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ nanocrystals: (a) $x = 0$, (b) $x = 0.01$, (c) $x = 0.03$, (d) $x = 0.05$, (e) $x = 0.07$ and (f) $x = 0.1$.

substitution. Also, segregation of impurities on the surface or grain boundary can suppress the growth of crystalline grain for $\text{Zn}_{1-x}\text{Co}_x\text{O}$ nanocrystals with high doping concentrations [19].

The morphology and phase structure of the samples were further studied by TEM. The typical TEM images of $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$ nanocrystals were presented in Fig. 3(a) and (b). Fig. 3(a) shows the low magnification TEM micrograph. The corresponding particle size distribution histogram of $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$ nanoparticles is given in Fig. 3(c), the average particle diameters were found to be approximately 15–20 nm, which is consistent with XRD results. A HRTEM image recorded from a particle is shown in Fig. 3(b). A nice crystallinity and clear lattice fringes can be observed, indicating that the nanocrystal is single crystalline. The lattice spacing between two adjacent lattice fringes is 2.8 Å, which corresponds to the interplanar spacing of (100) plane of hexagonal wurtzite ZnO.

### 3.2. Raman spectra of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ nanocrystals

Raman scattering is a powerful and nondestructive tool to investigate the microstructure, secondary phase segregation, and the local lattice vibrational properties for impurity doped semiconductors. Fig. 4 illustrates the unpolarized Raman spectra of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ nanocrystals with different Co concentrations.
Fig. 3. TEM images of Zn$_{0.95}$Co$_{0.05}$O nanocrystals: (a) low-magnification and (b) HRTEM images; (c) the particle-size distribution histogram of Zn$_{0.95}$Co$_{0.05}$O nanoparticles, evaluated from the corresponding TEM micrograph.
at room temperature. For Zn$_{1-x}$Co$_x$O nanocrystals with low Co concentrations ($x \leq 0.03$), similar Raman spectra are observed. As the characteristic mode of wurtzite crystal structure, the dominant peak at 432 cm$^{-1}$ is observed and can be assigned to the high frequency branch of E$_2$ mode of ZnO. The mode becomes weak with increasing Co concentration. According to the selection rules, the weak peaks at 323, 383, 565 cm$^{-1}$ can be assigned to E$_{2H}$–E$_{2L}$, A$_{1T}$ and A$_{1L}$/E$_{1L}$ modes, respectively [20,21]. As the concentration is above 0.03, four new additional modes (AM) at 479 cm$^{-1}$, 523 cm$^{-1}$, 612 cm$^{-1}$ and 678 cm$^{-1}$ are clearly observed, which can be attributed to E$_g$, F$_{2g}^{(1)}$, F$_{2g}^{(2)}$ and A$_{1g}$ symmetric phonon modes of Co$_3$O$_4$, respectively, implying that Co$_3$O$_4$ phase is segregated from ZnO nanocrystals [21]. Moreover, the AM around 540 cm$^{-1}$ is observed in Co-doped ZnO nanocrystals, which can be assigned to the quasi-LO mode due to the abundant shallow donor defects (zinc interstitials or oxygen vacancies) bounded on the tetrahedral Co sites, similar results have been reported by other groups [22,23].

It is suggested that some Co atoms can be incorporated into ZnO lattice and located at the substitutional sites at low Co concentration, impurity phases will be segregated from ZnO nanocrystals with high doping concentration.

3.3. Absorption and luminescence properties

In general, for Co impurities, optical absorption spectroscopy is considered an effective tool to reveal the electronic transitions which are sensitive to the local environment of the impurity and determine whether the impurity is incorporated into ZnO lattice [24]. Fig. 5 shows the UV–Vis absorption spectra of Zn$_{1-x}$Co$_x$O nanocrystals with different Co concentrations as well as Co$_3$O$_4$ powder prepared under the same conditions. Compared with the spectrum of undoped ZnO, three additional absorption peaks are observed at 566 nm, 609 nm and 654 nm for Co-doped ZnO nanocrystals, which are related to d–d transitions of Co$^{2+}$ in a tetrahedral crystal field and can be attributed to the $^4$A$_2$(F)$^2$E(G), $^4$A$_2$(F)$^4$T$_1$(P), and $^4$A$_2$(F)$^4$A$_1$(G), respectively, indicating that some Co$^{2+}$ ions are substituted for Zn$^{2+}$ ions in ZnO [14,25]. As the Co concentration increases, the absorbance intensity of the Co-related peaks between 550 nm and 700 nm is regularly strengthened and the absorption edge red shifts. The redshift of the ZnO bandgap after Co or Mn doping has been observed, which is generally attributed to the modification of bandgap due to sp–d exchange interactions. However, except for the excitonic peak at 340–370 nm related to ZnO semiconductor band-to-band transition, a weak additional peak at 400 nm is observed for Co-doped ZnO nanocrystals. In general, the absorption peaks of TM doped semiconductors are related to ligand-field, charge-transfer and semiconductor band-to-band transitions [13]. The weak additional peak at $\sim$400 nm can be assigned to sub-bandgap charge-transfer transitions in which the Co$^{2+}$ acts as the charge-transfer acceptor and the valence band serves as the
charge-transfer donor. The similar ligand-to-metal charge-transfer (LMCT) transition has been reported in Ni and Co-doped ZnO nanocrystals [13,26,27]. As revealed by XRD and Raman results, Co3O4 phase is segregated when the doping concentration is above 0.03. According to Fig. 5(b), Co3O4 black powder shows strong absorption bands in the whole UV–Vis range. Therefore, the redshift of the absorption edge can be attributed to the overlap of LMCT transition for Zn1-xCoxO nanocrystals with low Co concentration (x ≤ 0.03) and the contribution of Co3O4 for Zn1-xCoxO nanocrystals with high Co concentration.

The PL spectra of Zn1-xCoxO nanocrystals were measured at room temperature with an excitation wavelength of 325 nm, as shown in Fig. 6(a). The undoped ZnO nanocrystals exhibit a weak near band edge UV emission (NBE) at 380 nm and a broad strong band at 545 nm. Compared with the PL spectrum of undoped ZnO, Co doping induces fluorescent quenching, which is related to the unradiative process or additional transition process for the incorporation of Co into ZnO. Similar results were observed in some previous reports [14,28–30]. The position of the UV emission exhibits a blue shift (from 390 nm to 383 nm) as Co doping concentration increases, likely due to quantum confine effects [31]. Besides, the visible emission bands located at 440 nm, 585 nm and 685 nm are observed in all Co doped ZnO nanocrystals.

The visible emission bands of ZnO are generally attributed to electron transfer from the conductor band to defect levels (or impurity levels) in the forbidden band or from defect levels to the valence band or between different defect levels (or impurity levels). In order to understand the origins of the broad visible emission of ZnO, the PL spectra were measured under different excitation energies, as shown in Fig. 6(b). As the excitation wavelength increases from 330 nm to 400 nm, the asymmetric broad emission band changes from green (~545 nm) to yellow (~580 nm), indicating that the broad emission spectrum contains two bands in green and yellow region and the yellow emission can be effectively excitated by the energy below the bandgap.

According to the experimental and the theoretical results [32–34], a schematic diagram showing the energy levels of defects in ZnO lattice (such as interstitial zinc (Zni), oxide antisite defect (OZn), interstitial oxygen (Oi)) and Co2+ impurity level in a tetrahedral crystal field is drawn in Fig. 7. OZn defect level is located at ~2.38 eV below the conduction band and the Oi is located at ~0.9 eV above the valence band, which can act as deep acceptors [33]. Calculations indicate that Zni can act as a shallow donor and trap electrons, inducing effective transitions from the Zni energy level to the valence band and other deep levels [33,35]. The yellow emission observed in ZnO and Co-doped ZnO nanocrystals can be associated with recombination of trapped electrons in Zni defect level and deeply trapped holes in Oi, whereas the blue emission for doped ZnO nanocrystals is assigned to the transition between Zni defect level and valence band according to energy differences. The green emission is observed in
undoped ZnO nanocrystals and most of the green emission is quenched as the excitation energy decreases below the bandgap, which can be assigned to the transition from the conduction band to deep levels ($O_{Zn}$). Ionic radius of Co$^{2+}$ is close to that of Zn$^{2+}$ and Co$^{2+}$ ions can occupy the Zn sites. Since $O_{Zn}$ defects are often thermodynamically unstable at the high annealing temperature [36], Co$^{2+}$ ions are easier to substitute for $O_{Zn}$ sites in ZnO nanocrystals under annealing conditions. As a result, green emission was not observed in Co-doped ZnO nanocrystals.

The red emission at $\sim$685 nm can be observed in Co-doped ZnO nanocrystals, which is rarely observed in undoped ZnO. For the purpose of excluding the frequency multiplication of exciting light, the PL spectra of Co-doped ZnO samples were carried out at different excitation wavelengths. The red emissions are unchanged in shape and position, indicating Co doping can be considered the possible cause of the red emission in Co-doped ZnO nanocrystals, in agreement with the results of absorption spectra. This is consistent with the PL spectra obtained from the previous reports [37,38]. The crystal-field split energy levels of substitutional Co$^{2+}$ ions are shown in Fig. 7 (the red part). Based on the absorption spectra and PL spectral analysis, an electron transition mechanism is proposed as follows: electrons are excited to the excited states of Co$^{2+}$ under light excitation, and electrons located at the higher excited states can be tend to relax to a lower excited state. Since the distance between the lowest excited state ($^2E(G)$) and the basic state ($^4A_2(F)$) is large, electrons eventually return to

Fig. 6. (a) PL spectra of Zn$_{1-x}$Co$_x$O nanocrystals with different Co doping concentrations. The intensity of pure ZnO has been reduced 150 times. The excitation wavelength is 325 nm; (b) Excitation energy dependence of PL spectra of undoped ZnO.
ground state via radiative transition, resulting in emitting photons at a wavelength of 685 nm. For Zn$_{1-x}$Co$_x$O nanocrystals with high doping concentrations, the Co-related emission intensity decreases probably due to the segregation phase of Co$_3$O$_4$.

4. Conclusions

Zn$_{1-x}$Co$_x$O nanocrystals with different Co doping concentrations have been synthesized by a simple solution route followed by a calcining process. The analysis of XRD and Raman spectra reveals that Co$^{2+}$ ions are substituted for Zn$^{2+}$ ions in ZnO at a low Co concentration. The defect emissions in ZnO nanocrystals were modified by Co doping. In addition, the spectra related to transitions within the tetrahedral Co$^{2+}$ ions in the ZnO host crystal were also observed in absorption and luminescence spectra. Thus, the current method can be regarded as an effective technique to modulate the optical properties of ZnO nanocrystals.

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