

Synthesis and photoluminescent properties of ZnO:Cu/ZnO core/shell nanocrystals*

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ZnO:Cu/ZnO core/shell nanocrystals are synthesized by a two-step solution-phase process. The morphology, structure and optical properties of the samples are detected by scanning electron microscopy, Raman, absorption and luminescence spectroscopy. The increase of particle size confirms the growth of ZnO shell. The segregation of CuO phase observed in ZnO:Cu core is not detected in ZnO:Cu/ZnO core/shell nanocrystals from Raman spectra. It is suggested that some Cu ions can be segregated from ZnO nanocrystals, and the separated Cu ions can be incorporated inside ZnO shell after the growth of ZnO shell. The visible emission mechanism is discussed in detail, and the photoluminescence analysis indicates that the core/shell structure helps to eliminate the surface-related emission.

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The incorporation of impurity ions into ZnO can change its electronic structure, and then modify the electronic and optical properties^[1-3]. The emission spectra of ZnO:Cu nanostructures extend from ultraviolet (UV) to visible (Vis) region, which depends on the doping concentrations^[4], defects^[5] and excitation energy^[6]. Therefore, Cu doped ZnO can be considered as a promising candidate for light emitting devices.

One of the key problems for doped semiconductor nanocrystals is how to avoid the segregation of impurity and yield substitutional doping in nanocrystal lattice^[7]. Due to the high surface-to-volume ratio and the self-purification of nanocrystals^[8], a large part of dopants in ZnO nanostructures tend to locate near the surface, and repeatedly washing is insufficient to remove them^[9]. In addition, unpassivated surface sites may act as a nonradiative recombination way, which suppresses efficient luminescence. Therefore, the control of doped nanocrystal's surface has been a critical issue to achieve effective doping and obtain highly luminescent nanocrystals. This problem could be overcome partially by the core/shell

method. D. X. Jiang et al^[10] revealed that ZnO shell has a passivating effect on the surface states of ZnS:Mn core. W. T. Zhang^[11] found that Zn(OH)₂ shell can suppress the nonradiative recombination transitions in CdS:Mn nanocrystals core. Moreover, the growth of a ZnS shell on ZnS:Mn²⁺ nanocrystals resulted in an increase of photoluminescence (PL) intensity^[12]. However, most reports focus on the PL spectra related to surface state. Few papers are concerned about the doping efficiency for the core/shell structures of doped ZnO materials.

In this paper, ZnO:Cu/ZnO core/shell nanocrystals are synthesized by a two-step solution-phase process. The growth of undoped ZnO shell can eliminate the surface-related defects. In addition, the subsequent growth of ZnO shell around the doped ZnO nanocrystal core can cover the adsorbed dopants inside the newly formed nanocrystals, and the doping efficiency is enhanced. The Vis emission mechanism is explained in detail.

The detailed experimental procedures for ZnO:Cu nano-

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crystals with Cu doping concentration of 2% are as follows. The precursor salts (zinc acetate dihydrate ($\text{ZnAc}_2 \cdot 2\text{H}_2\text{O}$) and copper acetate tetrahydrate ($\text{CuAc}_2 \cdot 4\text{H}_2\text{O}$)) were dissolved in 55 mL absolute ethanol, and the total metal ion concentration was kept at 0.1 M. A sample of sodium hydroxide (NaOH, 1 M) dissolved in dry ethanol (25 mL) was added to the metal salt solution under vigorous stirring at 70 °C for 2 h.

The shell was synthesized according to the reported procedure^[13]. After ZnO:Cu particles were formed, 55 mL of 0.1 M $\text{ZnAc}_2 \cdot 2\text{H}_2\text{O}$ and 25 mL of 1 M NaOH diluted precursor solutions were alternately added to ZnO:Cu core suspension. According to Ostwald ripening theory^[14], the newly added Zn^{2+} and OH^- react at surface of ZnO:Cu core. Then the turbid reaction mixture was heated for 2 h at 70 °C, and a ZnO shell was formed around the ZnO:Cu core. The products were separated from the solution by filtration, washed two times with de-ionized water and three times with absolute ethanol, and then dried in air at 40 °C for 5 h to remove the residual solvent. In this paper, ZnO core, ZnO:Cu core and ZnO/ZnO core/shell structure were also prepared for comparison.

The morphologies of the samples are characterized by scanning electron microscopy (SEM) (JEOL/JSM 6700F NT). Raman spectra are acquired from LabRam micro-Raman spectrometer with the wavelength of 533 nm at room temperature. UV-Vis absorption spectra are recorded on a Hitachi 4100 UV-Vis spectrophotometer. PL and photoluminescence excitation (PLE) spectra are monitored by a spectrometer (FluoroLog 3, Horiba Jobin Yvon) using 450 W Xe lamp.

Fig.1 shows SEM images of ZnO, ZnO/ZnO, ZnO:Cu and ZnO:Cu/ZnO nanocrystals. An abundance of nearly spherical particles are recognized from all samples. As shown in Fig.1, the particle size of the samples without ZnO shell is

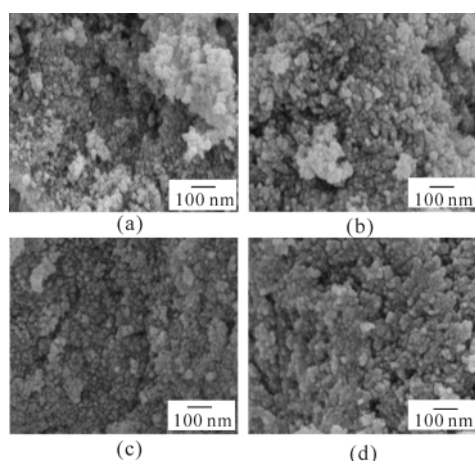


Fig.1 SEM images of (a) ZnO, (b) ZnO/ZnO, (c) ZnO:Cu and (d) ZnO:Cu/ZnO nanocrystals

smaller than that with ZnO shell. The increase of particle size is consistent with the formation of core/shell structure^[15], which indicates that the subsequent additions of Zn^{2+} and OH^- precursors followed by heat treatment can form a ZnO shell around ZnO:Cu nanocrystals.

Fig.2 illustrates the Raman spectra of ZnO, ZnO/ZnO, ZnO:Cu, ZnO:Cu/ZnO nanocrystals at room temperature. As the characteristic mode of wurtzite crystal structure, the dominant peak at 435 cm^{-1} is observed and can be assigned to the high frequency branch of E_2 mode of ZnO, which indicates that all samples possess hexagonal wurtzite structure. In comparison with the vibrational spectra of ZnO, the weak peaks at 99 cm^{-1} , 201 cm^{-1} , 324 cm^{-1} , 386 cm^{-1} , 580 cm^{-1} , 1087 cm^{-1} and 1153 cm^{-1} can be assigned to E_{2L} , $2\text{TA}/2E_{2L}$, $E_{2H}-E_{2L}$, A_{1T} , A_{1L} , TO+LO and $2A_{1L}/2E_{1L}/2\text{LO}$ modes, respectively^[16]. An additional mode (AM) at 295 cm^{-1} is observed in the spectra of ZnO:Cu nanocrystals, which can be attributed to A_g mode of CuO^[17], implying that CuO phase is segregated from ZnO nanocrystals. It is suggested that some Cu ions can be segregated from ZnO nanocrystals, and the separated Cu ions can be incorporated inside ZnO shell after the growth of ZnO shell.

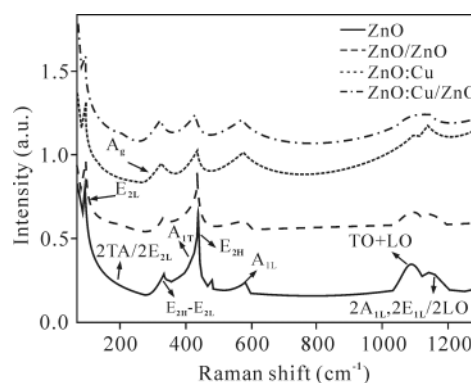


Fig.2 Raman spectra of ZnO, ZnO/ZnO, ZnO:Cu and ZnO:Cu/ZnO nanocrystals

From Fig.3, the absorption edges of all samples are located at about 375 nm (3.3 eV), which corresponds to the band gap energy of ZnO. The inset of Fig.3 shows a blue-shift of the absorption edge for the samples without ZnO shell with respect to that with ZnO shell, which indicates a size quantum effect. Compared with the spectra of undoped samples, wide absorption bands are observed in Vis region for ZnO:Cu and ZnO:Cu/ZnO nanocrystals. Since no evidence for impurity phase is detected in Raman spectra of ZnO:Cu/ZnO nanocrystals, the additional Vis absorption may be due to the incorporation of Cu ion into ZnO lattice^[18]. The difference of UV-Vis absorption spectra between ZnO:Cu

and ZnO:Cu/ZnO nanocrystals may be caused by the segregation of CuO phase.

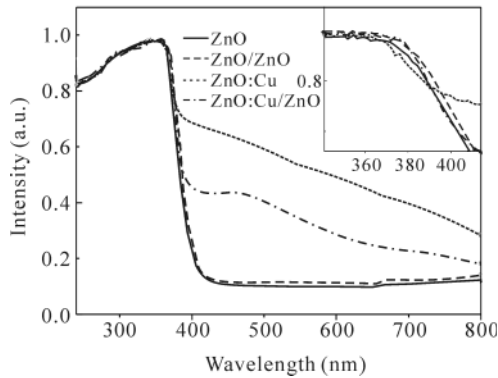


Fig.3 UV-Vis absorption spectra of ZnO, ZnO/ZnO, ZnO:Cu and ZnO:Cu/ZnO nanocrystals

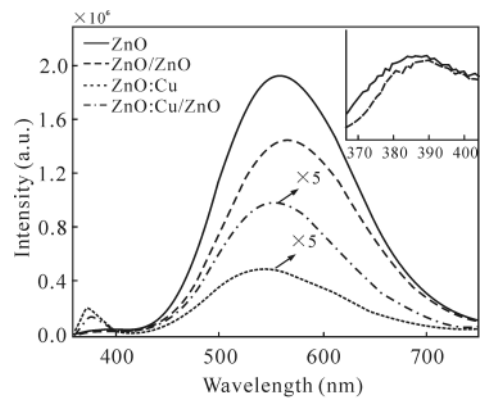
In Fig.4(a), PL spectra show two emissions of a near band edge UV emission (NBE) centered at about 380 nm (~ 3.3 eV) and a broad Vis emission located around 550 nm (~ 2.25 eV). Compared with the emission of ZnO nanoparticles, ZnO/ZnO shows an enhanced Vis emission, which suggests that the Vis emission of undoped ZnO may be generated from near-surface defects. In contrast, the Vis emission intensity of ZnO:Cu/ZnO nanocrystals is about 2 times larger than that of ZnO:Cu nanocrystals, indicating that the enhancement of Vis emission for ZnO:Cu/ZnO nanocrystals cannot be attributed to the surface state. The surface state of nanocrystals can be passivated after the growth of ZnO shell^[10-12]. On the other hand, the UV emission and Vis emission of the samples with ZnO shell are red-shifted compared with that of the samples without ZnO shell, which can be attributed to the increased size after the growth of shell. The results are consistent with the report by R. W. Xuan *et al*^[19].

In order to investigate the Vis emission band of the samples, room-temperature PL spectra of all samples are elaborately measured under different excitation energies. PLE spectra are obtained under different emission positions.

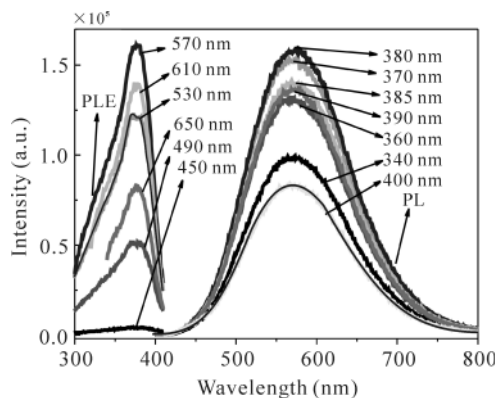
It can be seen from Fig.4(b) that the green emission (~ 556 nm) of undoped ZnO remains almost unchanged in their position under different excitation energies, suggesting one dominant component with fixed wavelengths. The PLE spectra of undoped sample indicate that the preferential excitation energy is below band-gap and the initial state is located slightly below the conduction band edge. As a result, the green emission can be attributed to the recombination of a delocalized electron in a shallow donor level with a deeply trapped hole, such as interstitial zinc and oxygen vacancies^[20].

As shown in PL spectra of ZnO:Cu/ZnO nanocrystals, when the excitation is below the band-edge energy, the emis-

sion position shifts to shorter wavelength and is accompanied by the appearance of blue emission, which suggests that the Vis emission of Cu doped ZnO nanocrystals consists of three components at least. The Gaussian fitting for Vis emission of ZnO:Cu/ZnO nanocrystals in Fig.4(d) clearly shows that three sub-bands are centered at about 450 nm, 527 nm and 583 nm. When the excitation energy is near the band gap, the blue and green emissions coexist with yellow emission, and a broad emission from 400 nm to 650 nm is formed. This interesting phenomenon indicates the emission of transitions involving different defects. As the excitation energy decreases below the band gap, most of the yellow emission is quenched, and the spectra are mainly composed of blue and green emissions with unchanged peak position. As a result, the observed blue-shift is due to the disappearance of the long-wavelength component of the emission with increasing excitation wavelength. The initial states of yellow emission could be confirmed as the conduction band, and the blue and green emissions might come from the recombination of electron from an energy level below the conduction band to a trap level. PLE spectra of ZnO:Cu/ZnO nanocrystals show that a peak is located at about 365 nm, which sharply drops at about 380 nm for emission in the range of 610–650 nm. A weak peak at 400 nm with a slowly dropping tail for emission in the range of 450–570 nm indicates that the initial state of



(a)



(b)

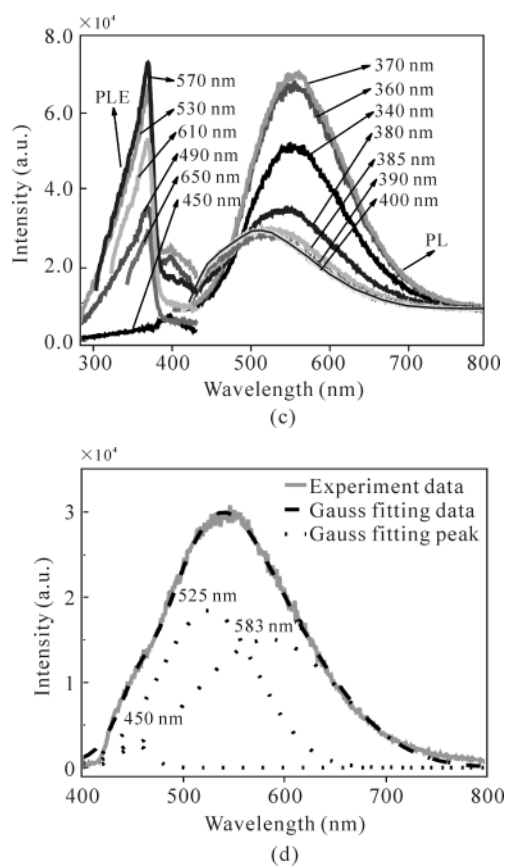


Fig.4 (a) Room-temperature PL spectra (The intensities of samples with doped ZnO are enlarged by 5 times. The inset shows the enlarged UV emission of undoped samples.); Emission-dependent PLE and excitation-dependent PL spectra of (b) ZnO/ZnO and (c) ZnO:Cu/ZnO core/shell nanocrystals; (d) Gaussian fitting curves of emission excited at 380 nm for ZnO:Cu/ZnO nanocrystals

blue and green emissions is probably located at about 0.2 eV below the conduction band. The substitutional Cu^{2+} was reported to be located at 0.1–0.19 eV below the conduction band and can act as a shallow donor^[6], so that Cu impurities might play a significant role in the origin of blue and green emissions for Cu doped ZnO nanocrystals. According to the earlier research^[21], the defect responsible for the yellow emission is not located at the surface. As a result, the broad Vis emissions of doped ZnO can be assigned to the substitutional Cu^{2+} and the defects inside ZnO lattice.

ZnO:Cu/ZnO core/shell nanocrystals with Cu doping concentration of 2% are synthesized by a solution-phase route. SEM results confirm the growth of ZnO shell. The surface coating of ZnO covers the adsorbed dopants within the newly formed

nanocrystals and helps to eliminate the surface-related defects. PL and PLE spectra reveal that the Vis emission of doped ZnO is from the substitutional Cu^{2+} and the defects inside ZnO lattice.

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