

Synthesis and photoluminescence of ZnS:Cu nanoparticles

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Abstract

The room-temperature photoluminescence (PL) of copper doped zinc sulfide (ZnS:Cu) nanoparticles were investigated. These ZnS:Cu nanoparticles were synthesized by a facile wet chemical method, with the copper concentration varying from 0 to 2 mol%. By Gaussian fitting, the PL spectrum of the undoped ZnS nanoparticles was deconvoluted into two blue luminescence peaks (centered at 411 nm and 455 nm, respectively), which both can be attributed to the recombination of the defect states of ZnS. But for the doped samples, a third peak at about 500 nm was also identified. This green luminescence originates from the recombination between the shallow donor level (sulfur vacancy) and the t_2 level of Cu^{2+} . With the increase of the Cu^{2+} concentration, the green emission peak is systematically shifted to longer wavelength. In addition, it was found that the overall photoluminescence intensity is decreased at the Cu^{2+} concentration of 2%. The concentration quenching of the luminescence may be caused by the formation of CuS compound.

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1. Introduction

In recent years, much effort has been devoted to the research of doped metal chalcogenide nanostructured materials. This kind of nanomaterials exhibits unusual physical and chemical properties in comparison with their bulk materials, such as size-dependent variation of the band gap energy [1,2]. Furthermore, impurity ions doped into these nanostructures can influence the electronic structure and transition probabilities [3]. In particular, when doped with magnetic ions (e.g. Mn^{2+}), these materials can produce unique magnetic and magneto-optical properties and provide unparalleled opportunities for the new field of spintronics [4].

As an important II–VI semiconductor material, ZnS is chemically more stable and technologically better than

other chalcogenides (such as ZnSe), so it is considered to be a promising host material. Transitional metal ions (e.g. Mn^{2+} [5,6] and Cu^{2+} [7,8]) and rare earth ions (e.g. Eu^{2+} [2,9]) have been incorporated into ZnS nanostructures by thermal evaporation, sol–gel processing, coprecipitation, microemulsion, etc. These doped ZnS semiconductor materials have a wide range of applications in electroluminescence devices, phosphors, light emitting displays, and optical sensors. Accordingly, special attention has been paid to their luminescence properties. In ZnS:Mn nanoparticles, an orange luminescence has been well documented, which is attributed to the $^4\text{T}_1-^6\text{A}_1$ transition of Mn^{2+} ions excited via energy transfer from the host ZnS [10]. Similar intraionic emission from the characteristic $4f^7-4f^65d^1$ transition of Eu^{2+} was also observed in ZnS:Eu nanoparticles [2]. However, in the case of nano-sized ZnS:Cu, the luminescence properties are still controversial. Two emission bands (blue and green) were often observed together in the same sample, such as 420 and 520 nm by Lee et al. [8] and 460 and 507 nm by Xu et al.

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[9]. On the other hand, a single emission peak was also observed at 480 nm [7] or at 415 nm [11]. Recently, Bol et al. reported a red emission around 600 nm in ZnS:Cu nanoparticles and assigned it to the recombination between a deeply trapped electron and Cu^{2+} [12].

Kinds and concentrations of dopants play key roles in luminescence efficiency and the positions of emission bands of semiconductor nanoparticles, thus influencing their practical applications. Therefore, it is very important to investigate how the dopant concentration of doped semiconductor nanoparticles affects optical properties from the viewpoints of basic physics and applications. Research work on ZnS:Cu nanoparticles, including material preparation [7,8] and property characterization [9,11–13], has been carried out. However, as far as we know, studies of the effect of Cu^{2+} concentration on the luminescence of ZnS nanoparticles are very limited. In this paper, we reported the synthesis and optical studies of ZnS:Cu nanoparticles. The influence of the concentration of copper ions used in the synthesis on the luminescence was investigated and the origin of the luminescence observed was also discussed.

2. Experimental

The synthesis of ZnS:Cu nanoparticles was carried out by a chemical method at room temperature. The principle is the precipitation reaction of metal ions and sulfur ions in solution. First, zinc acetate and copper acetate were dissolved in the mixed medium of deionized water and methanol. The concentrations of copper ions were adjusted by controlling the quantity of copper acetate in the above mixture, varying from 0.5% to 2% (in molar ratio of copper ions to zinc ions). α -methacrylic acid (MA) was also added to the reaction medium as the capping agent. Then, water/methanol binary solution of sodium sulfide was slowly

dropped into the above mixture, along with the continuous stirring under nitrogen protection. The formed nanoparticles were centrifugally separated from the solution. After repeatedly washed with deionized water and methanol and then dried under vacuum, the powder samples of ZnS nanoparticles doped with different copper concentrations were obtained. As a comparison, pure ZnS nanoparticles were also prepared using the above method.

The X-ray diffraction (XRD) patterns were recorded to characterize the phase and structure of the nanoparticles using a Rigaku DMax-RB powder diffractometer with a rotating anode and a Cu $K\alpha 1$ radiation source ($\lambda = 1.5406 \text{ \AA}$) at 40 kV and 150 mA. The sizes and morphology of the nanoparticles were observed by a JEM-2010 high-resolution transmission electron microscope (HRTEM) operated at 200 kV. Optical absorption was performed on an Agilent HP1100 diode-array UV-visible spectrophotom-

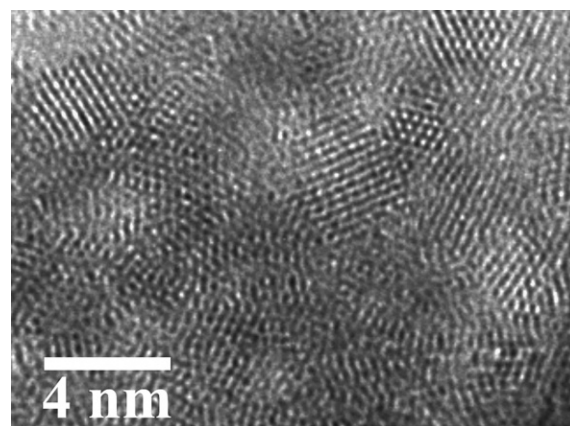


Fig. 2. Representative high-resolution transmission electron microscope image of the ZnS:Cu nanoparticles (0.5% doped).

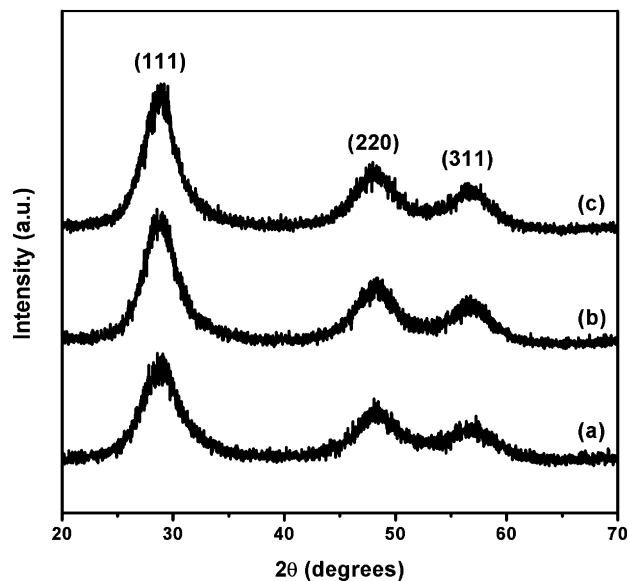


Fig. 1. X-ray diffraction patterns of the ZnS nanoparticles with Cu^{2+} concentrations of (a) 0.5%, (b) 1%, and (c) 2%.

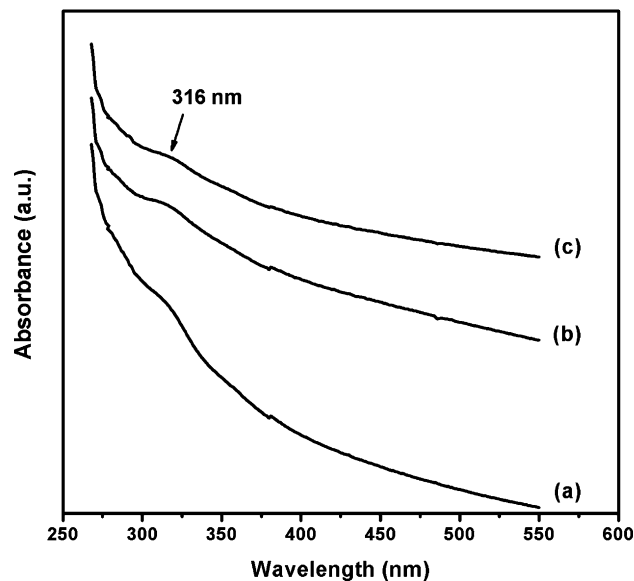


Fig. 3. UV-visible absorption spectra of the ZnS nanoparticles with Cu^{2+} concentrations of (a) 0.5%, (b) 1%, and (c) 2%.

eter. Room temperature photoluminescence (PL) of the powder samples was measured to characterize the luminescence properties of the nanoparticles, using a Jobin Yvon H25 fluorescence spectrophotometer with the 325 nm line of a He–Cd laser as excitation source.

3. Results and discussion

The XRD patterns of the ZnS:Cu nanoparticles, shown in Fig. 1, reveal the cubic zinc blende structure of ZnS (JCPDS No. 05-0566). The three peaks correspond to the (111), (220), and (311) lattice planes, respectively. No characteristic peaks of copper impurity (such as CuS, CuO) were detected, at least within the resolution limit of the diffractometer. From the XRD patterns, the broadening of the diffraction peaks of the nanoparticles is obvious, which is characteristic of nanosized materials. A representative HRTEM image of a ZnS:Cu sample (0.5% doped) is

displayed in Fig. 2. The mean size of these nanoparticles from HRTEM observation is about 3.5 nm. In the HRTEM image, lattice fringes can be clearly observed, which indicates that the particles are crystalline. The HRTEM images of the ZnS nanoparticles doped with 1% and 2% Cu also show similar sizes and morphology.

Fig. 3 exhibits the UV–visible absorption spectra of the ZnS:Cu nanoparticles. An absorption shoulder at about 316 nm (3.92 eV) was observed and its position shows little change with the variation of the doping concentration. This is because the concentrations of Cu^{2+} ions incorporated into the nanoparticles are small and do not change the particle size under similar synthesis conditions. The band gap energy is increased compared to that (~ 3.6 eV) of bulk ZnS; the enlargement of the band gap can be attributed to the quantum confinement effect of the ZnS:Cu nanostructures. According to the effective mass approximation theory [14], the band gap energy of 3.92 eV corresponds

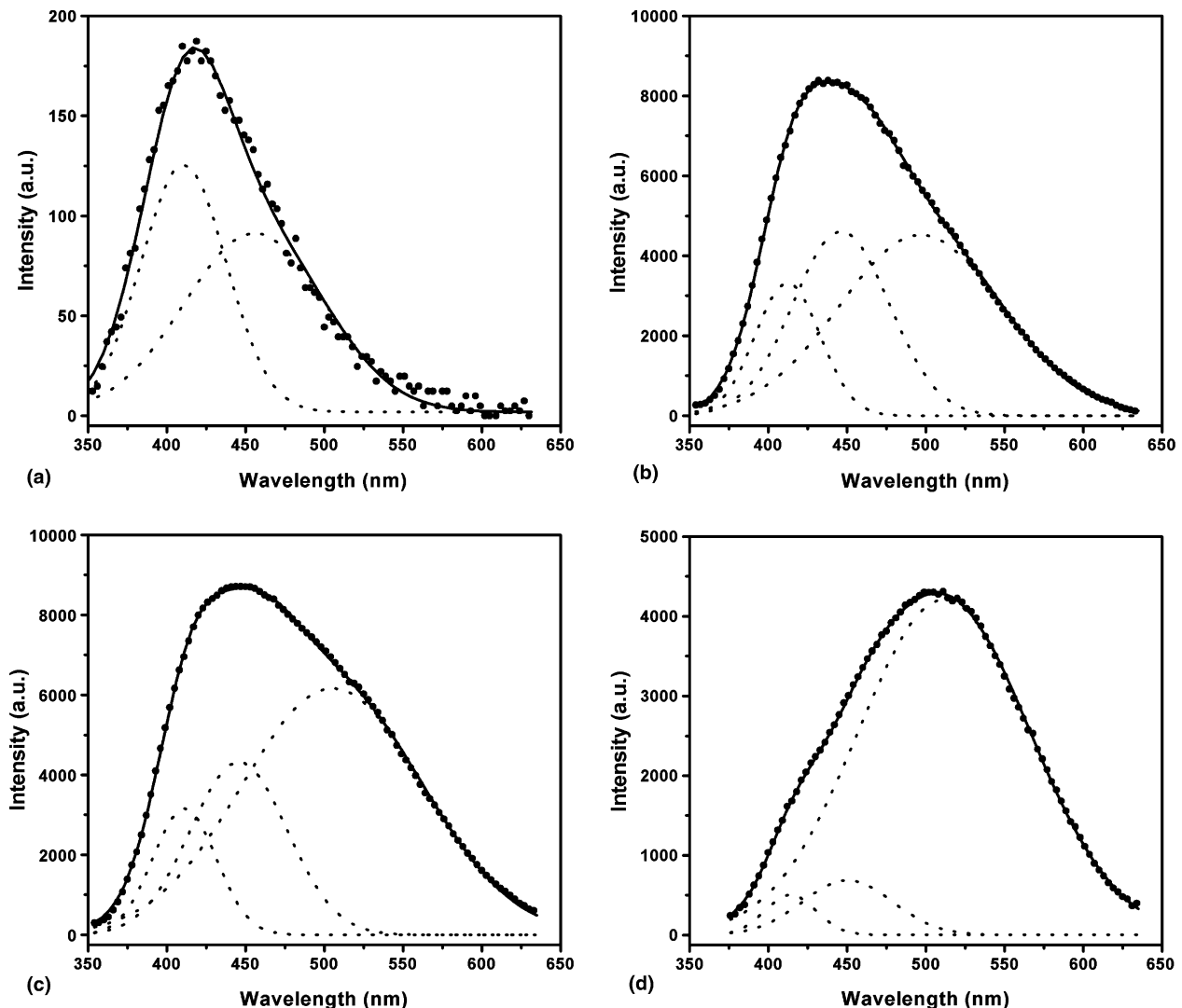


Fig. 4. Room temperature photoluminescence spectra of the ZnS nanoparticles with Cu^{2+} concentrations (a) 0%, (b) 0.5%, (c) 1%, and (d) 2%. The experimental data are shown in solid circles. The dashed lines are the individual components by Gaussian fitting, and the solid lines are the sum of individual fitting lines.

to particles with the average particle size of about 3.8 nm. This is in agreement with the results of HRTEM observation.

The room temperature PL spectra of the ZnS nanoparticles and the ZnS:Cu nanoparticles are shown in Fig. 4. The spectra are broad and asymmetric, so it should consist of more than one component. Gaussian curve fitting was applied to deconvolute the PL curves, and the fitting results are listed in Table 1. The PL spectrum of the undoped ZnS nanoparticles was deconvoluted into two weak peaks, which are centered at 411 and 455 nm, respectively. For the ZnS:Cu nanoparticles, besides these two blue emission peaks, a third peak was also identified in the green region.

The PL peak at 410 nm has been known due to the recombination between the sulfur-vacancy-related donor and the valence band [8]. As shown in Table 1, the peak position of this blue emission does not change with the increase of the Cu^{2+} concentration, which indicates that the energy level of sulfur vacancy relative to the valence band nearly keeps constant. For the emission peak at about 450 nm, different origins were proposed. Xu et al. [9] attributed the emission peak to the transition between the conduction band of ZnS and the t_2 energy level of excited Cu^{2+} (d^9) in the ZnS band gap. However, the undoped sample also shows such a blue peak (Fig. 4(a)). By inductively coupled plasma atomic absorption spectroscopy (ICP-AES), no copper or other impurities were found in the undoped sample. In addition, the emission peak position is insensitive to the concentration of Cu^{2+} ions (Table 1). So, it is suggested that in our case, the peak at 450 nm should result from native defect states, but not from impurity states related with Cu dopants. In ZnS nanoparticles [15,16] and ZnMnS nanobelts [5], the similar luminescence around this wavelength (450 nm) was also observed and attributed to the trap states emission of ZnS, related with native zinc vacancy. From Fig. 4, it can be seen that the peak intensities at 411 nm and 455 nm for the undoped sample are much smaller than those for the doped samples. It can be explained by the effect of doping. As analyzed above, these two peaks are related with native defects (e.g. sulfur vacancy). When Cu^{2+} ions are doped into ZnS nanoparticles, more defect states will be introduced. Therefore, it is reasonable that these two defect-related peak intensities are enhanced for the doped samples compared with the undoped sample.

In ZnS:Cu nanoparticles, a green emission peak around 500 nm was observed, in agreement with earlier results in

ZnS:Cu nanostructures [9]. The green emission arises from the recombination between the shallow donor level (sulfur vacancy) and the t_2 level of Cu^{2+} . It should be mentioned here that our prepared CuS nanoparticles do not show any luminescence under UV radiation. Therefore, the observed green emission originates from Cu^{2+} ions that are embedded in the ZnS matrix and substitute Zn^{2+} ions in ZnS nanoparticles. With the increase of the Cu^{2+} concentration, the green emission peak position is systematically shifted to longer wavelength (from 497 to 512 nm). As aforementioned, the energy level of sulfur vacancy relative to the valence band nearly keeps constant in these samples despite the variation of the Cu^{2+} concentration. So it can be concluded that the t_2 energy level of Cu^{2+} ions is farther from the valence band with increasing Cu^{2+} concentrations.

Based on the PL results observed, the schematic energy level diagram of ZnS:Cu nanoparticles can be depicted as shown in Fig. 5. This figure explains the emission mechanism of ZnS:Cu nanoparticles and illustrates the above assignment.

As shown in Fig. 4, the relative intensity of the overall emission (including blue and green peaks) reaches the maximum at the doping concentration of 1%. When the doping concentration is 2%, the luminescence intensity is diminished. In Eu-doped GaN [17], a similar concentration-quenching phenomenon was also observed, which was mainly attributed to the formation of EuN compound. In our case, the decrease of the luminescence intensity at the Cu^{2+} concentration of 2% may also be caused by the formation of CuS, though the XRD measurement did not detect the existence of the copper sulfide phase. One evidence is that the nanocrystalline ZnS:Cu powder color is changed from almost white to grey when the doping con-

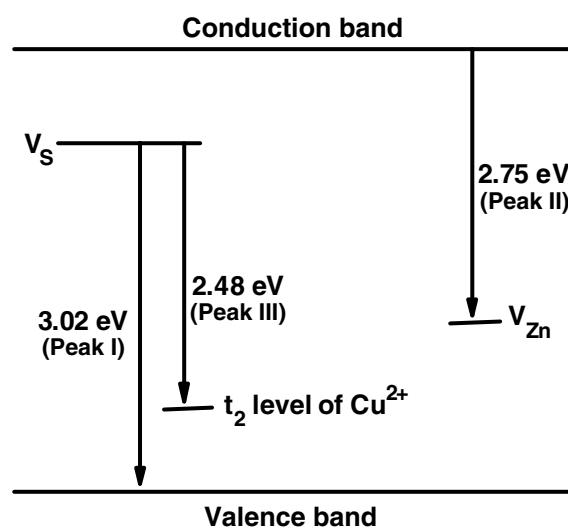


Fig. 5. Schematic energy level diagram showing the emission mechanism in the ZnS:Cu nanoparticles. Here, V_S stands for sulfur vacancy and V_{Zn} for zinc vacancy.

Table 1
Photoluminescence peak positions in the ZnS and ZnS:Cu nanoparticles

Cu concentration (mol%)	PL peak positions		
	Peak I (nm)	Peak II (nm)	Peak III (nm)
0	411	455	–
0.5	412	446	497
1	411	446	505
2	414	450	512

centration is 2%. CuS particles not only act as nonradiative recombination centers, but also reduce the number of Cu^{2+} ions that are optically active luminescence centers in ZnS nanoparticles. Therefore, the emission intensity is considerably decreased when the Cu^{2+} concentration is 2%, as shown in Fig. 4.

4. Conclusions

In summary, we have synthesized ZnS:Cu nanoparticles of about 3.5 nm by a simple wet chemical route. The XRD patterns exhibited the cubic zinc blende structure of ZnS for all the samples and no other crystalline phase was detected. Due to the quantum confinement effect, the band gap of the nanoparticles is increased compared with bulk material. The PL spectra of the doped samples are broad and asymmetric and can be deconvoluted into three Gaussian peaks. Of these, a green luminescence peak is related with copper impurities while two blue luminescence peaks can be attributed to native defects of ZnS. With increasing Cu^{2+} concentrations, the green emission peak is systematically shifted to longer wavelength. Further, the overall PL intensity is decreased at the Cu^{2+} concentration of 2%. The concentration quenching of the luminescence may be caused by the formation of CuS compound.

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