Chemical synthesis and characterization of Cu doped ZnS nano-powder

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In the past few years, II–VI compounds semiconductor nanocrystal have received much interest because their optical properties are different from the corresponding bulk crystals [1, 2]. Among II–VI compounds, ZnS is one of the most promising host materials for the production of commercial thin film phosphors for electroluminescent (EL) device application [3–7]. Since its absorption and emission lie in the ultraviolet regime, the studies of its small size particles did not evoke much interest until the 1980s. In 1994, Bhargava and Gallagher first synthesized ZnS semiconductor microcrystallites doped with Mn^{2+} ions; they found that the photoluminescence of Mn^{2+} doped in ZnS nanoparticles had much higher quantum efficiency than bulk crystals [8]. Hereafter, the metal doped ZnS nanoparticles have received increasing interest.

Recently, many methods have been developed in preparation of Cu doped ZnS nanopowder [9, 10]. In this paper, we report a new chemical synthesis method for preparation of Cu doped ZnS nanopowder as shown in Fig. 1. This process concluded two steps: First, selection to synthesize different lengths of the zinc methacrylate polymer by adjusting the molar ratio of mercaptoacetic acid to monomer of the methacrylic acid; second, the polymer reaction with sodium sulfide and cupric sulfate, giving the Cu doped ZnS nanopowder. During formation of the nanoparticles, the nanoparticles were capped by the methacrylic polymer, which passivated the surface atoms, eliminated the energy levels inside of gap, and increased the luminescence intensity. The size of nanoparticles can be well controlled from 1.8 nm to 3 nm by adjusting the molar ratio of mercaptoacetic acid to monomer of methacrylic acid. The production of Cu doped ZnS nanopowder was also characterized by TEM, XRD and PL.

Methacrylic acid (99%) monomers were purified by distillation under reduced pressure prior to use. The cupric sulfate (99%), zinc acetate dihydrate (99%), sodium sulfide (99%), potassium persulfate (99.5%) and mercaptoacetic acid ($HSCH_2COOH$) (85%) were used without further purification. All of the chemicals were purchased from Beijing chemical reagent corporation.

To synthesize Cu doped ZnS nanopowder, 40×10^{-6} m^3 of water, 0.03 mol of zinc acetate, and 5.5×10^{-6} m^3 (6.49×10^{-4} molar) of methacrylic acid were added to a three-neck flask equipped with condenser, then heated and stirred. When the temperature increased about 60 °C, 40×10^{-6} m^3 of 0.005 M potassium persulfate aqueous solution and 10^{-5} m^3 of 0.032 M (3.2×10^{-6} molar) mercaptoacetic acid aqueous solution were added, respectively. The temperature was kept at 80 °C for 1 h. 20×10^{-6} m^3 of 0.008 M $CuSO_4$ aqueous solution was added into reactor vessel and stirred for 5 min. 40×10^{-6} m^3 of 0.8 M sodium sulfide aqueous solution was dropped into the reactor at a constant rate. When the Na_2S aqueous solution was complete, the reaction was continued for an additional 30 min at 80 °C. The powder was well separated from the solution by centrifuging, rinsed with methanol and dried in vacuum. The Cu doped ZnS nano-powder was obtained.

The PL spectra of Cu doped ZnS nanopowder were recorded with a Hitachi F-4500 fluorescence spectrophotometer. The spectra were obtained by exciting the sample with 368 nm wavelength at room temperature. X-ray powder diffraction was performed on the Cu doped ZnS powder on a Rigaku RU-200B rotaflex diffractometer using Cu Kα $\lambda = 0.15406$ nm. TEM

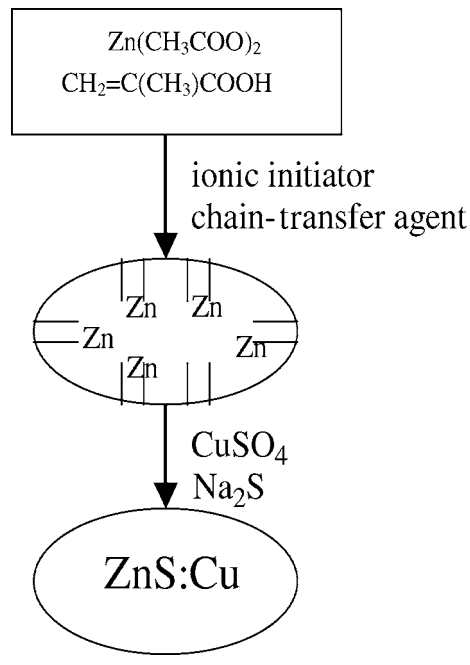
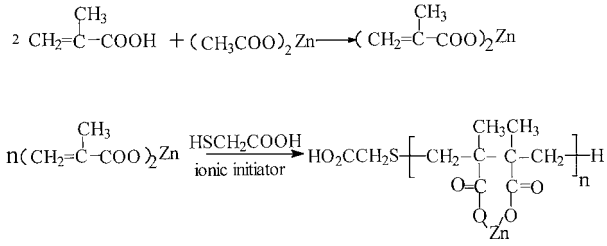


Figure 1 Schematic experimental procedure for the preparation of Cu doped ZnS nano-powder.

images were taken on a Jeol-2010 transmission electron microscope operated at 200 kV.

The synthesis process, can be described as follows



where the chain-transfer agent is mercaptoacetic acid, the ionic initiator is potassium persulfate. In this experiment, the amount of methacrylic acid is always slightly bigger than that of zinc acetate and the surplus methacrylic acid meets the reaction requirement of the $CuSO_4$. During formation of the ZnS : Cu nanoparticles, the zinc methacrylate polymer changes into methacrylic polymer. The methacrylic polymer capped the nanoparticles and then prevented the aggregation of the nanoparticles. At the same time, the methacrylic polymer passivated the surface of the nanoparticles. The Cu doped ZnS nanoparticle size can be well controlled by adjusting the molar ratio of mercaptoacetic acid to monomer of the methacrylic acid. The molar ratio of mercaptoacetic acid to monomer of the methacrylic acid enables control of the average length of zinc methacrylate polymer. By changing the molar ratio, different lengths of zinc methacrylate polymer can be formed. When different lengths of zinc methacrylate polymer react with sodium sulfide, we can obtain different size nanoparticles.

Fig. 2a shows a typical TEM image of Cu doped ZnS nanoparticles. The molar ratio of mercaptoacetic acid to monomer of the methacrylic acid is 1 : 200. The Cu doped ZnS nanoparticles are well dispersed as shown in Fig. 2a. The individual Cu doped ZnS nanoparticles size is about 2 nm. By changing the molar ratio of mercaptoacetic acid to monomer of the methacrylic acid to 1 : 360, the formed Cu doped ZnS nanoparticle size distribution changes, as shown in Fig. 2b. The Cu doped ZnS nanoparticles are also well dispersed and the size of individual nanoparticles is about 2.5 nm. (Fig. 2b)

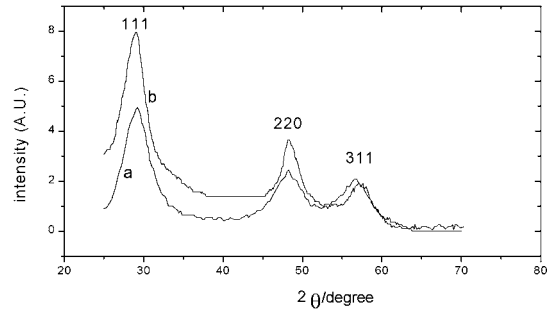


Figure 3 X-ray diffraction pattern of Cu doped ZnS nanopowder. Fine broadening measurements gave average crystal diameters of: (a) 2 nm, (b) 2.5 nm.

The Cu doped ZnS nanoparticles was characterized by X-ray powder diffraction. Which showed a perfect match with the diffraction pattern published in the literature [11]. The X-ray diffraction patterns of Cu doped ZnS nanoparticles of different size are shown in Fig. 3. From Fig. 3, we can clearly find that the Cu doped ZnS nanopowder shows considerable broadening in the X-ray pattern. This broadening of the diffraction peaks is primarily due to the finite size of the nanocrystallites. The diffraction peaks from zinc blende index as (111), (220) and (311). To calculate the nanoparticle diameter from the width of the line in the XRD spectrum, the Scherrer formula was used. According to the calculation, the Cu doped ZnS nanoparticle size are about 2.1 nm, 2.7 nm, respectively. The results agree well with the TEM result (Fig. 2a and b).

Room temperature PL spectra of Cu doped ZnS nanoparticles of different size are shown in Fig. 4. Fig. 4 indicated that different sizes of Cu doped ZnS nanoparticles have the same peak wavelength at 466 nm. It is more important to note that PL intensity of Cu doped ZnS nanoparticles increase with decreasing crystallite size. The enhanced PL intensity may be due to quantum size effect. Similar phenomena was also observed in the Mn doped ZnS nanoparticle [11]. The peak wavelength at 466 nm clearly blue shift compared with the peak wavelength of bulk Cu doped ZnS. The blue luminescence of copper is due to a transition from the conduction band of ZnS to the "t_2" level of excited Cu^{2+} in the ZnS band gap [12].

In summary, a new chemical synthesis method for preparation of Cu doped ZnS nanopowder was

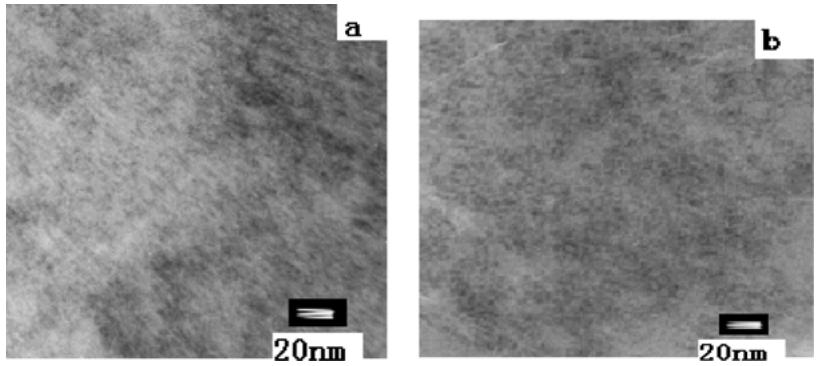


Figure 2 TEM images of Cu doped ZnS nanopowder. The molar ratio of mercaptoacetic acid to monomer of the methacrylic acid is 1 : 200 (a) and 1 : 360 (b), respectively.

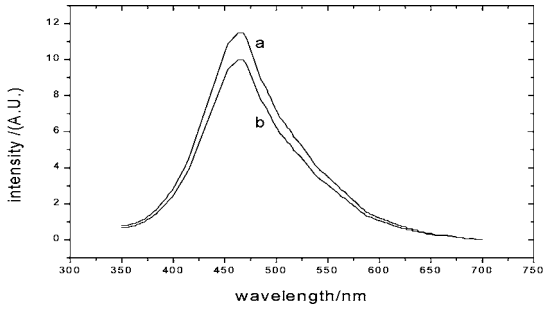


Figure 4 PL spectra of Cu doped ZnS nanopowder. The molar ratio of mercaptoacetic acid to monomer of the methacrylic acid is 1 : 200.

investigated. The size of the ZnS : Cu nanoparticle from 1.8 nm to 3 nm can be well controlled by adjusting the molar ratio of mercaptoacetic acid to monomer of the methacrylic acid. The TEM images reveal that the ZnS : Cu nanoparticles have uniform size distribution. XRD results demonstrated that the ZnS : Cu nano-powder have zinc blende crystal structure. The PL spectra indicated that PL intensity of Cu doped ZnS nanoparticles increases with decreasing crystallite size. The enhanced PL intensity was explained by the quantum size effect. The chemical synthesis technique can be easily extended to prepare other metal doped ZnS nanopowders such as ZnS : Mn, ZnS : Cu : Al etc. only need to select suitable materials.

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