SIZE DEPENDENT PHOTOLUMINESCENCE PROPERTIES OF Mn-DOPED ZnS NANOCRYSTALS

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Mn-doped ZnS nanocrystals were synthesized via a facile hydrothermal method with the assistant of propanetriol. The structure characterization of the resulting samples was investigated by means of X-ray powder diffraction (XRD). Results indicated that the diameters of the Mn-doped ZnS nanocrystals were in the range of 3.5-4.5 nm. More importantly, we found that propanetriol played a crucial role during the synthesis of controlled Mn-doped ZnS nanocrystalline size. It has been found that nanocrystalline size of Mn-doped ZnS increased with the amount of propanetriol into a reactant mixture. The tunability of the photoluminescence properties of Mn-doped ZnS was identified to be related to the nanocrystalline size. The results will be significant in fabrication of controlled nanocrystalline structure based on various optical divices applications.

1. Introduction

Recently, nanocrystalline semiconductor have received much attention due to their novel optical and electronical properties arising from their unique quantum nature [1-4]. These materials are different from those of bulk semiconductors. ZnS is a II-VI compound semiconductor with direct and wide band gap of 3.68 eV and widely used as a phosphor in optical devices[5-10]. In addition Mn-doped ZnS had attracted much interest due to their photoluminescence properties in comparison with the bulk materials [11, 12].

There have been few reports on the synthesis and characterization of Mn-doped ZnS nanocrystals [3, 4, 13] since Bhargava and his co-workers reported the photoluminescence properties of Mn-doped ZnS nanocrystals prepared in at room temperature chemical process [6]. Recently, various synthesis routes have been employed to synthesis Mn-doped ZnS nanocrystals. Yang et al. have presented a method to synthesis Mn-doped ZnS nanocrystals by a competitive reaction chemistry, where p-thiocresol, a surface capping organic species, is used as an inhibitor of the crystal growht [14]. Gan et al. had prepared Mn-doped ZnS photoluminescence nanomaterials in an inverse micromulsion at room temperature as well as a hydrothermal condition [8].These methods have severals advantages like controlled size and large scale yield. However, in spite of the above successes, the ability to control the nanocrystalline size of Mn-doped ZnS is still difficult in proper synthesis conditions.There is little work on the photoluminescence properties studies of Mn-doped ZnS nanocrystals via a facile hydrothermal method with the assistant of propanetriol.

In this paper, we reported the synthesis and characterization of Mn-doped ZnS prepared by a facile hydrothermal method with the assistant of propanetriol.

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2. Experimental section

2.1 Synthesis of Mn-doped ZnS nanocrystals

All chemicals are analytical-grade reagents without further purification. In a typical experiment, 0.04 mol of zinc acetate, 0.2 mol of urea and 0.01 mol of manganese acetate were dissolved in a different volume ratio of propanetriol and deionized water mixed solution. The mixed solution was further magnetically stirred for 1 h. The soluton was then transferred into a Teflon-lined autoclave of 100 ml capacity. The autoclave was heated to 220 °C for 14 h. After being cooled to room temperature, the white powders were collected and washed several times with ethanol and distilled deionized water to remove the impurities and then dried at 60 °C for 24 h.

2.2 Characterization of Mn-doped ZnS nanocrystals

Phase structure of Mn-doped ZnS nanocrystals was measured with Cu-Kα radiation source (λ=0.154056 nm) at 40 KV and 30 mA. The absorption spectra of Mn-doped ZnS nanocrystals was measured in Shimadzu UV-4100 (UV-Visible-NIR spectrophotometer) equipped with an integrating sphere. The PL characterization of Mn-doped ZnS nanocrystals was recorded on a FLS920 fluorescence spectrometer

3. Results and discussion

3.1 XRD analysis

The X-ray diffraction patterns of the as-synesized Mn-doped ZnS nanocrystals by hydrothermal method were presented in Fig.1. The diffraction peaks at 2θ values of 28.6°, 47.5°, 56.3° corresponding to the (111), (220) and (311) planes of cubic ZnS (JCPDS No.05-0566). The broadening of the XRD peaks shows the typical nanocrystalline characterization of the samples. Additionally, no diffraction peaks from manganese impurities were observed. The nanocrystalline size is estimated according to the Debey-Scherer Equation:

$$D = \frac{k\lambda}{\beta \cos\theta} \tag{1}$$

Where D is the mean grain size, k the constant (shape factor, appromately 1), λ the X-ray wavelength (1.54056 Å for Cu-Kα), β the full width at half maxium (FWHM) of the diffraction peak and θ the Bragg diffraction angle. According to the FWHM of the most intense peak (111) plane, the average crystalline sizes for different propanetriol concerntration were estimated to be 3.5 nm for 2%, 4.0 nm for 6%, 4.5 nm for 10%, respectively.
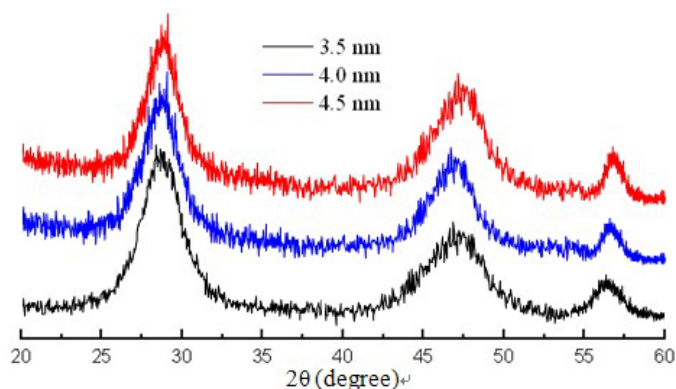

Fig.1. Powder X-ray diffractgrams of a size series of Mn-doped ZnS nanocrystals.

3.2 UV-Vis measurement

Fig.2 shows the UV-Vis absorption spectra for all samples of Mn-doped ZnS nanocrystals. The excitonic peak is found to be blue-shifted with decrease in nanocrystalline size (307.868 nm-295.178 nm), which could be attributed to the confinement effects due to the Mn-doped ZnS nanocrystalline size is comparable to the excitation Bohr radius, e.g. ca. 5 nm for ZnS. The relationship between the adsorption coefficient and the incident photon energy of semiconductors are based on the following equation.

$$\alpha(h\frac{c}{\lambda}) \sim (h\frac{c}{\lambda} - E_g)^n \qquad (2)$$

Where α is absorption coefficient, h is Planck's constant, c is the velocity of light, λ is wavelength, and E_g is the optical band gap. Through calculating, the optical band gap of the nanocrystalline size is about 4.20 eV (295.178 nm) for 3.5 nm, 4.15 eV (298.985 nm) for 4.0 nm, and 4.03 eV (307.868 nm) for 4.5 nm, respectively. Much research had been performed to calculate the blue shift for ZnS nanoparticles in the form of a colloidal solution[15]. The results showed that our experimental results were also in good agreement with the reported values.
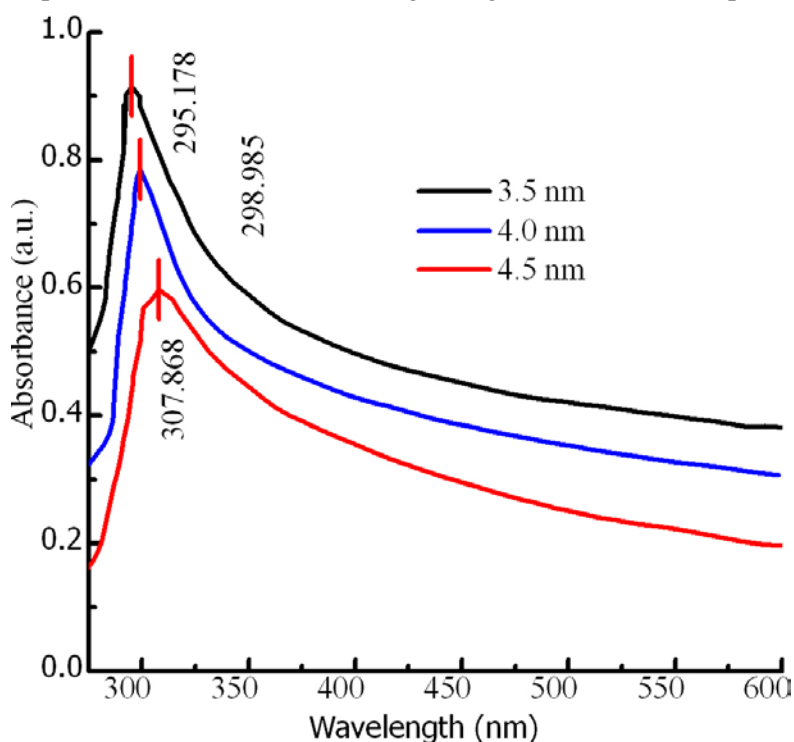

Fig.2. Optical absorption spectra for Mn-doped ZnS nanocrystals showing the red shift associated with increased nanocrystal size.

3.3 Photoluminescence properties of Mn-doped nanocrystals

Fig. 3 shows the excitation spectrum for an emission peak of 580 nm and peaks at 315 nm. The excitation spectrum showed that the Mn-doped ZnS nanocrystals exhibited a widened, but well-defined band gap which means a narrow size distribution. Since ZnS had a broadband absorption, excitation spectrum is pronounced in finding the excitation wavelengths at which it has

maximum emission. To study the luminescence properties quantitatively, the photoluminescence spectra of Mn-doped nanocrystals specimens of different nanocrystalline size for an excitation wavelength of 315 nm are shown in Fig. 4. The photoluminescence efficiency of nanocrystals can be determined $\eta=(1+\beta D^2)^{-1}$, where D is the volume of a nanocrystal and β is related to radiative and non-radiative decay time. Therefore, the photoluminescence efficiency of nanocrystals increased with decreasing nanocrystalline size, which is in good agree with our experimental results.
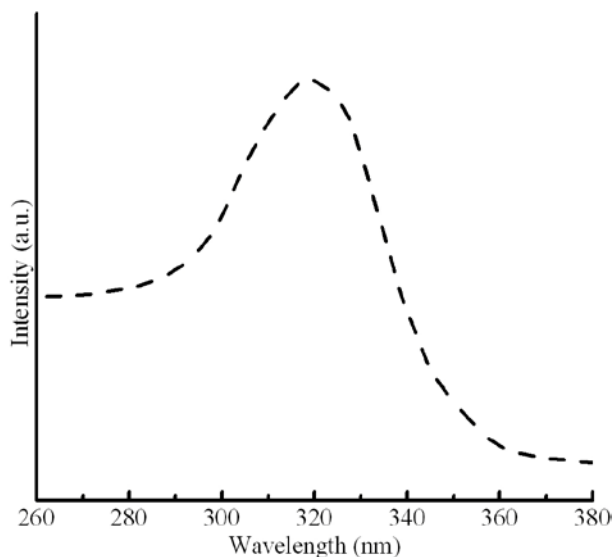

Fig. 3. Excitation spectrum of Mn-doped ZnS nanocrystals for an emission of 580 nm.

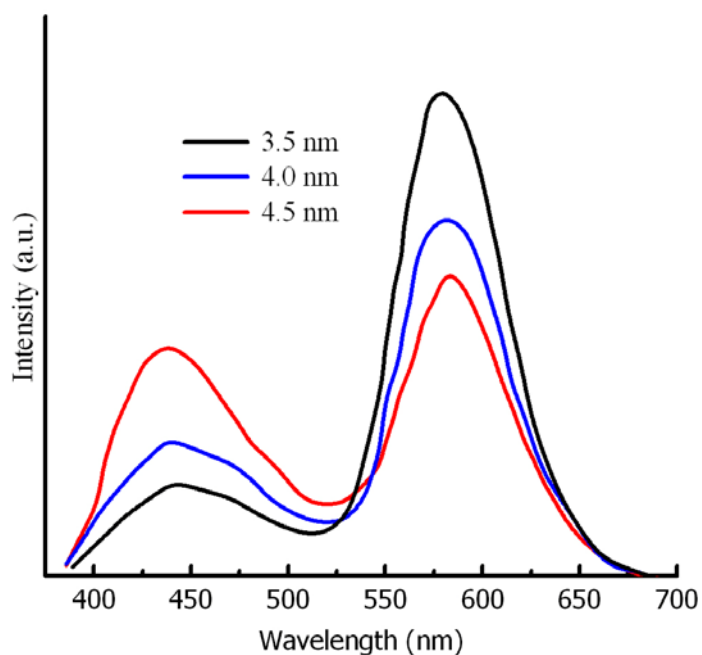## 3.3 Photoluminescence properties of Mn-doped ZnS nanocrystal

Fig.4. Photoluminescence spectra of Mn-doped ZnS nanocrystals of different nanocrystal size for an excitation wavelength

4. Conclusions

In summary, a size dependent photoluminecience properties of different Mn-doped ZnS nanocrystalline size was investigated. Nanocrystalline size of Mn-doped ZnS increased with the amount of propanetriol into a reactant mixture. The correlation between the photoluminescence properties and nanocrystalline size allows us to reconstruct the size curves from photoluminescence spectroscopy. Our studies may provide new possibilities of tailoring the size in the Mn-doped ZnS nanocrysalline structure thereby photoluminescence properties with the controlled amount of dopants in the matrix. The understanding of this result will be significant in fabrication of controlled nanocrystalline structure based on various optical divices applications.

Acknowledgements

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