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Synthesis and photoluminescence of water-soluble Mn^{2+}-doped ZnS quantum dots

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ABSTRACT

The water-soluble Mn^{2+}-doped ZnS quantum dots (Mn:ZnS d-dots) were synthesized by using thioglycolic acid (TGA) as stabilizer in aqueous solutions in air, and characterized by X-ray powder diffraction (XRD), UV–vis absorption spectra and photoluminescence (PL) emission spectroscopy. The sizes of Mn:ZnS d-dots were determined to be about 2 nm using XRD measurements and the UV–vis absorption spectra. It was found that the Mn^{2+} $^4T_1 \rightarrow {}^6A_1$ emission intensity of Mn:ZnS d-dots significantly increased with the increase of Mn^{2+} concentration, and showed a maximum when Mn^{2+} doping content was 1.5%. If Mn^{2+} concentration continued to increase, namely more than 1.5%, the Mn^{2+} $^4T_1 \rightarrow {}^6A_1$ emission intensity would decrease. In addition, the effects of TGA/(Zn + Mn) molar ratio on PL were investigated. It was found that the peak intensity ratio of Mn^{2+} $^4T_1 \rightarrow {}^6A_1$ emission to defect-states emission showed a maximum when the TGA/(Zn + Mn) molar ratio was equal to 1.8.

1. Introduction

Semiconductor nanocrystals, or quantum dots (q-dots), with CdSe ones as the workhorse, have been widely explored as biomedical labeling reagents since 1998 [1–4]. However, the small-ensemble Stokes shift of intrinsic q-dot emitters made self-quenching. In addition, experimental results indicated that any leakage of cadmium from the nanocrystals would be toxic and fatal to a biological system [5], and cadmium-containing products were eventually environmentally problematic. Recently, Peng and co-workers [6–8] reported that doped quantum dots (e.g. Mn:ZnSe d-dots) could not only replace cadmium in CdSe quantum dots with zinc, but also overcome a couple of intrinsic disadvantages of undoped quantum dots emitters, that is, strong self-quenching caused by their small-ensemble Stokes shift (energy difference between absorption spectrum and emission band) [9,10] and sensitivity to thermal, chemical, and photochemical disturbances [11,12]. Mn^{2+}-doped ZnS nanocrystals have been extensively investigated for use in various applications other than biomedical labeling, such as displays, sensors, and lasers [13–15]. In addition, the luminescent lifetime of Mn^{2+}-doped ZnS nanocrystals was ca. 1 ms. Such a long lifetime made the luminescence from the nanocrystal readily distinguishable from the background luminescence. Therefore, Mn^{2+}-doped ZnS nanocrystals could be potential candidates as fluorescent labeling agents, especially in biology [16].

To be a suitable bio-labeling agent, the nanocrystals should have high luminescent efficiency, water-solubilization, and biocompatibility. Water-soluble semiconductor nanocrystals could be obtained mainly by two different methods. The first way was to replace the surface-capping molecules on the particles prepared by the TOPO (trioctylphosphine oxide) method with water-soluble thiols [17]. However, after the substitution of the surface-capping molecules by hydrophilic molecules, the nanoparticle photoluminescence (PL) decreased markedly [17]. The second method was to directly synthesize semiconductor nanocrystals in aqueous solution using water-soluble stabilizers such as thiols [18]. The second method became a popular recipe for making water-soluble nanoparticles. It was generally believed that the preparation should be conducted in inert or reduced atmospheres because oxygen in the air could oxidize the nanoparticles and quench the luminescence. However, Liu et al. [19] reported that highly luminescent water-soluble CdTe nanoparticles could be synthesized in air and their luminescence efficiency was comparable to or higher than that of particles made in nitrogen. In this paper, water-soluble Mn^{2+}-doped ZnS quantum dots (Mn:ZnS d-dots) were prepared by using thioglycolic acid (TGA) as stabilizer in aqueous solution in air. The effects of the concentration of Mn^{2+} ions and the TGA/(Zn + Mn) molar ratio on the luminescence were investigated.

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2. Experimental

2.1. Chemicals

All chemicals used were of analytical grade. $Zn(CH_3COO)_2{\cdot}2H_2O$, $Mn(CH_3COO)_2{\cdot}2H_2O$, $Na_2S{\cdot}9H_2O$, and thioglycolic acid were obtained from Shanghai Chemical Reagents Company and used as received. High-purity water with a resistivity of 18.2 MΩ/cm was used for preparation of all aqueous solutions.

2.2. Synthesis of water-soluble Mn:ZnS d-dots

The water-soluble Mn:ZnS d-dots were synthesized by using thioglycolic acid as stabilizer in aqueous solution in air. In a typical experiment, aqueous stock solutions (0.1 M) of $Zn(CH_3COO)_2{\cdot}2H_2O$, $Mn(CH_3COO)_2{\cdot}2H_2O$, and Na_2S were freshly prepared. Zn^{2+} and Mn^{2+} solutions were mixed (0, 1, 1.5, 2, 2.5, and 3% Mn), and an appropriate amount of thioglycolic acid was added into the mixture under stirring. The pH was adjusted to 4.5, and an appropriate amount of 0.1 M Na_2S solution was quickly added into the mixture under vigorously stirring. Then the reaction mixture was heated at 80 °C for 120 min.

2.3. Characterization

The X-ray diffraction (XRD) patterns of the synthesized samples were obtained by a D/max-γA diffractometer using Cu Kα radiation (λ = 0.15418 nm). UV–vis absorption spectra were recorded with a UV–vis scanning spectrophotometer (Shimadzu UV-2450). The photoluminescence spectra of the samples were recorded with a Fluorescence Spectrophotometer F-4500.

3. Results and discussion

3.1. XRD analysis of Mn:ZnS d-dots

The XRD patterns of Mn:ZnS d-dots were shown in Fig. 1. These diffraction features appearing at 28.5°, 47.5°, and 56.3° corresponded to the (1 1 1), (2 2 0), and (3 1 1) planes of cubic zinc blende structure, which was very consistent with the values in the standard card (JCPDS No. 77-2100). No diffraction peaks from manganese impurities were detected. In addition, the broadening of the diffraction peaks of all the Mn:ZnS d-dots were obvious, which was characteristic of nanocrystal. The averaged crystallite sizes D was determined according to the Scherrer equation $D = k\lambda/\beta\cos\theta$ [20], where k was a constant (shape factor, about 0.9), λ was the X-ray wavelength (0.15418 nm), β was the full width at half maximum (FWHM) of the diffraction line, and θ was the diffraction angle. Based on the full width at half-maximum of (1 1 1) zinc blende reflection, the averaged crystallite sizes of Mn:ZnS d-dots doped with different Mn^{2+} concentration (0, 1.5 and 3%) were estimated to be 1.96, 2.04 and 2.11 nm, respectively.

3.2. Absorption spectra of Mn:ZnS d-dots

Fig. 2 showed the UV–vis absorption spectra of Mn:ZnS d-dots doped with different Mn^{2+} concentration. Mn:ZnS d-dots doped with different Mn^{2+} concentration (0, 1.5 and 3%) were at 310, 315, and 320 nm, respectively. All samples presented blue shift in comparison to bulk ZnS (340 nm). By using an experiential expression [21], the mean size of the Mn:ZnS d-dots were calculated to be 1.94, 2.03 and 2.12 nm, respectively, which were consistent with XRD results.

3.3. Photoluminescence spectra of Mn:ZnS d-dots

3.3.1. Effect of Mn^{2+} concentration

Fig. 3 showed the room temperature photoluminescence spectra of Mn:ZnS d-dots doped with different Mn^{2+} concentration under 340 nm excitation. It was found that the PL spectra of undoped samples showed only one emission band at about 460 nm, which could be assigned to the radiative recombination involving defect states in the ZnS nanocrystals [22]. For all the doped samples, two different emission bands dominated the PL spectra. The first emission band at about 460 nm also existed in the PL spectrum of the undoped ZnS nanocrystals, this emission band should indeed originate from the host ZnS but not from Mn^{2+} ions. The second emission band was centered at about 585 nm, which was due to $^4T_1 \rightarrow {}^6A_1$ transition within the 3d shell of Mn^{2+} [23]. When Mn^{2+} ions were incorporated into the ZnS lattice and substituted for host cation sites, the mixing between the s–p electrons of the host ZnS and the d electrons of Mn^{2+} occurred and made the forbidden transition of $^4T_1 \rightarrow {}^6A_1$ partially allowed,

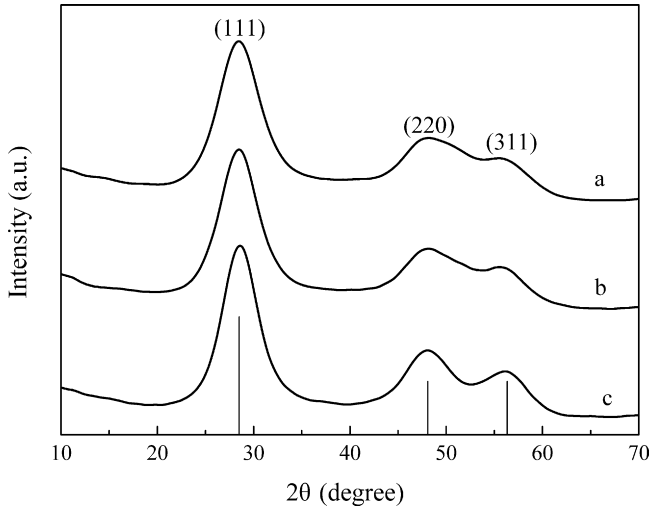

Fig. 1. X-ray diffraction patterns of Mn:ZnS d-dots doped with different Mn^{2+} concentration: (a) undoped, (b) 1.5%, and (c) 3%. The vertical lines denote the diffraction peaks of bulk ZnS with the cubic zinc blende structure (JCPDS No. 05-0566).

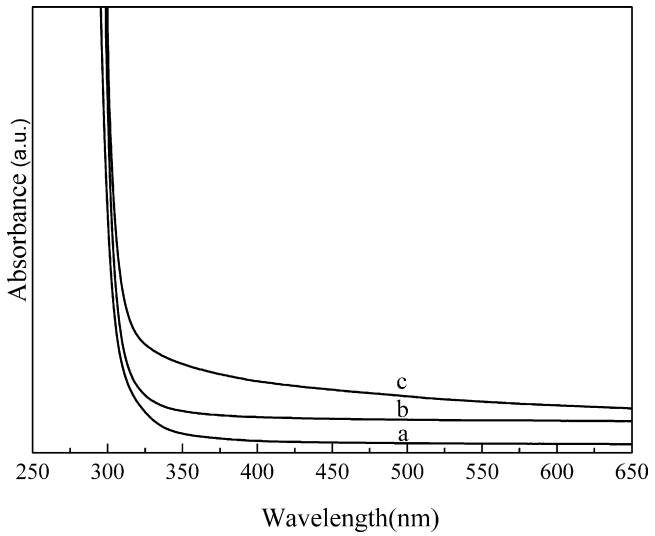

Fig. 2. The absorption spectra of Mn:ZnS d-dots doped with different Mn^{2+} concentration: (a) undoped, (b) 1.5%, and (c) 3%.