Size influence on the fluorescence decay time of ZnS:Mn^{2+} nanocrystals*

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ZnS:Mn^{2+} nanocrystals (NCs) with particle size from 1.9 nm to 3.2 nm are synthesized via chemical precipitation method with different [S^{2-}]/[Zn^{2+}] ratios. The size−dependent decay for Mn emission exhibits a double exponential behavior. And two lifetime values, in millisecond time domain, can both be shortened with size increasing, which is attributed to enhanced interaction between host and Mn^{2+} impurity. A molecular structure model is proposed to interpret the tendency of two lifetime components, which is correlated to the number of S vacancy (V_s) defects around Mn^{2+}.

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Semiconductor nanocrystals (NCs) play a promising role in electronic and optical devices, which stimulate research on their chemical properties, physical properties and microstructure[1,2]. How the microstructure influences the optical properties of NCs is an active area of research. The optical properties of NCs by tailoring the local environment of lattice may depend on size, shape and dopants under different preparation conditions[3-6]. The experimental observation suggested that tunable emission from red to blue region can be obtained in different sizes of CdSe NCs by separating nucleation and growth stages[7]. For different Eu-doped ZnO NCs including spherical, hexagonal and clubbed shapes, which are prepared by three solution-based approaches, the absorption spectrum shows red shift due to quantum confinement effects[8]. The intended dopants can act as recombination centers and exhibit rich luminescence behavior. Sameer Sapra et al observed a more rapid decay of defect-state recombination of ZnS NCs with a uniform diameter of 1.6 nm as the concentration of Mn^{2+} increased[9]. They considered that the number of Mn^{2+} in a nanocrystal alters the nonradiative energy transferred from defect states to Mn ions excited states. Furthermore, the size dependence of the radiative decay rates for the Mn^{2+}: ZnSe samples was investigated by Chenli Gan et al[10]. They owed two fast decay components to the emission tails from the host ZnSe NCs and from the surface-trap states or the self-activated luminescence due to Mn ion pairs, respectively. But the correlation between the microstructure and decay behavior has not been concerned.

The fluorescence decay time is an easily measured parameter to reveal the influence of host on energy levels of optical active centers and the mechanism of energy transfer. In the present work, various sizes of ZnS:Mn^{2+} NCs are synthesized using different molar ratios of [S^{2-}]/[Zn^{2+}]. To understand the effects of the particle size and microenvironment such as defects on luminescence behaviors, decay curves for Mn^{2+} of ZnS:Mn^{2+} NCs are investigated.

Chemical precipitation method is used to prepare various sizes of ZnS:Mn^{2+} NCs with [S^{2-}]/[Zn^{2+}] ratio in the range of 0.5 to 3, which was reported in our previous work[11]. X-ray diffraction (XRD) patterns are recorded on a Rigaku 2500/PC diffractometer using Cu Kα radiation (1.542 Å). Photoluminescence (PL) spectra and fluorescence decay at room temperature are performed with Horiba Jobin Yvon FluoroLog-3 fluorescence spectrophotometer under the exciting wavelength of 335 nm. The light sources are xenon lamp with 450 W for PL spectra and flash xenon lamp with maxi-

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mum repetition rate of 30 Hz for fluorescence decay, respectively.

Fig.1(a) shows XRD profiles of ZnS:Mn^{2+} NCs with different [S^{2-}]/[Zn^{2+}] ratios. It is observed that three diffraction peaks correspond to (1 1 1), (2 2 0) and (3 1 1) lattice planes, in agreement with bulk ZnS (cubic zinc blende, JCPDS No. 05-0566). The broad diffraction peaks for all samples are indicative of the ZnS particles with small size. Estimating from Debye-Scherrer formula, the average particle size of samples changes from about 1.9 nm to 3.2 nm as the [S^{2-}]/[Zn^{2+}] ratio increases from 0.5 to 3, which is consistent with the result reported by Suyver et al[12]. The increase of particle size may be mainly caused by the promotion of growth rate with the S-containing precursor increaseing[13]. PL spectra with different particle sizes under the excitation at 335 nm are shown in Fig.1(b). A broad emission centered around 585 nm is ascribed to the $^4T_1 \rightarrow {}^6A_1$ transition of Mn^{2+}.

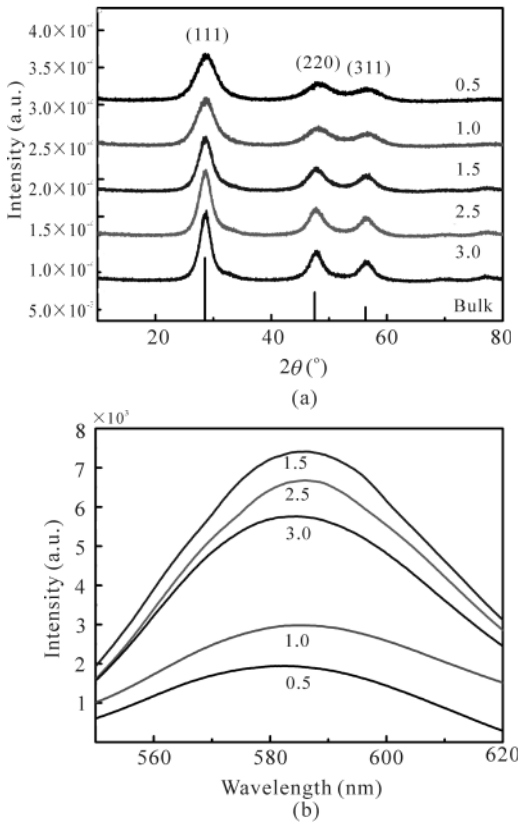

Fig.1(a) XRD patterns of ZnS:Mn^{2+} NCs with different [S^{2-}]/[Zn^{2+}] ratios; (b) Room temperature PL spectra of Mn^{2+} in ZnS:Mn^{2+} NCs with different particle sizes

Fig.2(a) shows the decay curves of Mn emission from ZnS:Mn^{2+} NCs with different particle sizes. The double exponential fitting of each curve provides a short lifetime (τ_1) and a long lifetime (τ_2) for all samples. Referring to Fig.2(a), two lifetimes, which are in millisecond time, are plotted as a function of particle size, as shown in Fig.2(b). Both lifetimes of Mn^{2+} decrease with particle size from 1.9 nm to 3.2 nm, whereas there is little change with particle size above 2.4 nm. Kelly Sooklal[14] suggested two local environments for Mn^{2+} in ZnS, which are "inside" and "outside", are closely related to particle size of NCs and could affect photophysical properties. For ZnS:Mn^{2+} NCs with small sizes prepared by insufficiency of S-containing precursor, there exists a weak interaction between host and Mn ions because most of Mn^{2+} ions are on the surface of NCs [14].With more additional S-containing precursor, the particle size increases and more Mn^{2+} ions are buried and encapsulated inside ZnS host. As a result, the interaction between ZnS host and Mn^{2+} impurity is strengthened[15]. According to standard perturbation theory[16], the recombination probability of Mn^{2+} emission can be expressed as

$$1/\tau = (a + b\xi)^2 , \quad (1)$$

where ξ represents the spin-orbit interaction between host material and active ions, and the constant a depends on the spin-orbit interaction of impurities. The lifetime shortening

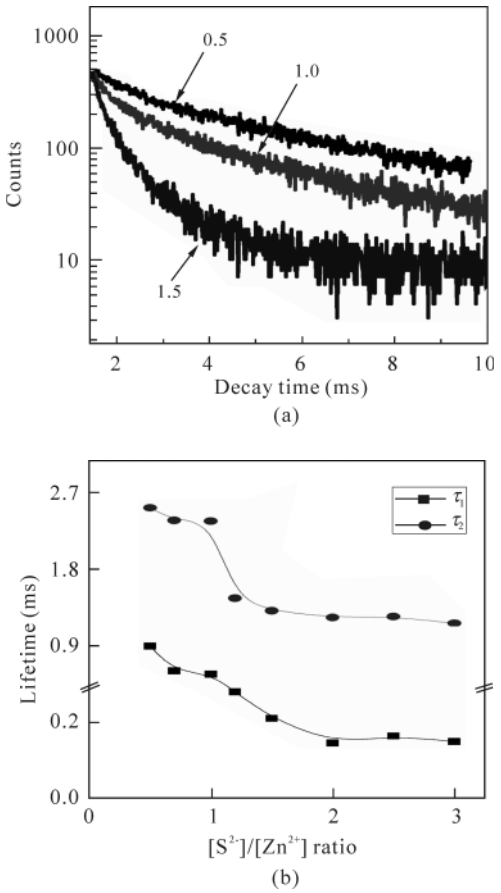

Fig.2(a) Decay curves (λ_{ex} = 335 nm, λ_{em} = 585 nm) of Mn emission in ZnS:Mn NCs with different particle sizes; (b) Short lifetime (τ_1) and long lifetime (τ_2) of Mn emission with different particle sizes fitted from Fig.2(a)

of Mn^{2+} can be attributed to the strengthened interaction between ZnS host and Mn^{2+} impurity, which is increased with the particle size.

To further understand the influence of particle size on decay time of ZnS:Mn^{2+} NCs, two fractional contributions to emission intensity from Mn^{2+} are plotted as a function of particle size in Fig.3. With the particle size increasing, short lifetime (τ_1) component increases, while long lifetime (τ_2) component decreases. As is well known, the electrons can be nonradiative relaxed from the conduction band or shallow S vacancy (V_s) defect donor level to the excited-state of Mn^{2+} for ZnS:Mn[17]. The lifetime of luminescence center is usually sensitive to its neighboring lattice environment[18]. Considering preparation method in this study, it could be imaginable that the fractional contribution to Mn^{2+} decay intensity is related to V_s defects around Mn^{2+}. We ascribe the two lifetime components to two types of Mn^{2+} in different lattice environments, such as the number of V_s or S^{2-} around Mn^{2+}. To reveal the local environment around Mn^{2+} impurities with different particle sizes, a molecular structure model correlated to the number of V_s defects (including four situations) is proposed in the inset of Fig.3. As the size increases with more S-containing precursor added, the number of V_s defects reduces. The proportions of situations I and II decrease, whereas those of situations III and IV increase, which is associated with the variation of fractional contribution to Mn^{2+} decay intensity. The short lifetime (τ_1) component can be ascribed to Mn^{2+} centers with less number of V_s (situations III and IV) around them, while the long lifetime (τ_2) component is ascribed to Mn^{2+} centers with more V_s (situations I and II).

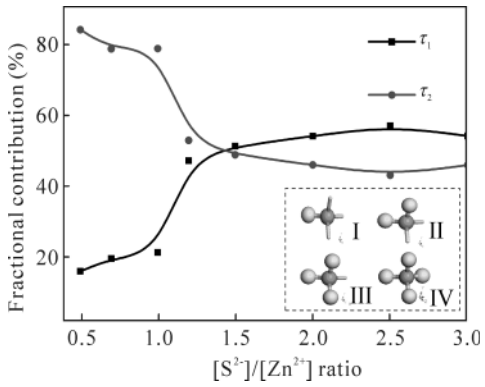

Fig.3 Two fractional contributions to Mn^{2+} decay intensity with different particle sizes (The inset displays the molecular structure models correlated to the number of V_s defects. The central ball, sideward ball and the stick represent cations, anions and chemical bonds, respectively.)

In summary, different sizes of ZnS:Mn^{2+} NCs are prepared by chemical precipitation method with different precursor molar ratios of [S^{2-}]/[Zn^{2+}]. XRD patterns exhibit that the sizes of ZnS:Mn^{2+} NCs increase from 1.9 nm to 3.2 nm with the [S^{2-}]/[Zn^{2+}] ratio from 0.5 to 3. As the particle sizes increase, the short lifetime (τ_1) and long lifetime (τ_2) of Mn^{2+} emission both decrease. The discussion indicates that the particle size of ZnS:Mn^{2+} NCs affects the interaction between ZnS host and Mn^{2+} impurity, and then affects the decay time of Mn^{2+}. By the molecular structure model which is correlated to the number of V_s defects, the short lifetime (τ_1) component is ascribed to Mn^{2+} centers with less number of V_s around them, whereas the long lifetime (τ_2) component is ascribed to Mn^{2+} centers with more V_s.

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