

Fluorescence lifetime of Mn-doped ZnSe quantum dots with size dependence

Chenli Gan,¹ Yanpeng Zhang,¹ David Battaglia,² Xiaogang Peng,² and Min Xiao^{1,a)}

¹Department of Physics, University of Arkansas, Fayetteville, Arkansas 72701, USA

²Department of Chemistry and Biochemistry, University of Arkansas, Fayetteville, Arkansas 72701, USA

(Received 7 November 2007; accepted 23 May 2008; published online 18 June 2008)

Radiative lifetimes of high quality Mn:ZnSe nanocrystals synthesized by nucleation-doping method are experimentally measured at wavelength near 580 nm. The slow decay rate in millisecond time scale is identified as the radiative decay from the 4T_1 metastable excited state of Mn^{2+} ions embedded in the ZnSe nanocrystals. Also, two fast decay components are measured at this wavelength with much lower intensities, which can be attributed to the emission tails from the host ZnSe nanocrystals and from the surface-trap states or the self-activated luminescence due to Mn ion pairs, respectively. Size dependences of the radiative decay rates for the Mn:ZnSe samples are measured. © 2008 American Institute of Physics. [DOI: 10.1063/1.2945274]

Transition metal doped semiconductor nanocrystals (*d*-dots) are of great interest for both fundamental research and technical applications. For technical applications, *d*-dots without heavy metal ions are expected to be a new generation of emissive nanocrystals¹⁻³ (NCs) for light-emitting diodes, lasers, and biomedical labeling and also potential materials for diluted magnetic semiconductors.^{4,5} For fundamental science, it is interesting to study how the quantum size effect would influence the luminescent properties of the Mn^{2+} ions in the semiconductor (such as ZnS) crystal field in the nanometer size regime. Bhargava *et al.*^{6,7} studied the luminescent properties of the Mn-doped ZnS NCs and reported that Mn^{2+} ions in the NCs can yield high luminescent efficiency with decay lifetime five orders of magnitude shorter than in the bulk size materials (previously measured to be in the millisecond time scale). The radiation transition from the lowest-excited level 4T_1 (spin 3/2) to the ground state (spin 5/2) in the Mn^{2+} ions is spin forbidden, so the oscillator strength is very small, which leads to the luminescence lifetime to be in the millisecond time scale. Bhargava *et al.* suggested that the existence of the strong hybridization of *s-p* electrons of the ZnS host and *d* electrons of the Mn impurity results in the lifetime shortening and the fast energy transfer to the Mn^{2+} ions makes enhancement in quantum yield of the Mn^{2+} ion emission.^{6,7}

However, this work of Bhargava *et al.*^{6,7} was challenged later by several other groups represented by the work of Bol and Meijerink,⁸ who reported that the Mn^{2+} ion emission of ZnS NCs does not show a spectacular shortening of the decay time when the particle size decreases. Also a similar radiative lifetime (~ 1.7 ms) of the Mn^{2+} emission in CdS NCs was observed by Chamarro *et al.*⁹ On the other hand, Sooklal *et al.*¹⁰ measured nanosecond decay times in Mn:ZnS NCs and Ito *et al.*¹¹ reported lifetime in microsecond time scale in Mn^{2+} :ZnTe NCs. A comparison of the energy levels of Mn^{2+} ions in bulk and in nanosized ZnS crystals shows no significant change in the degree of mixing between the *s-p* state of ZnS and the $3d$ state of the Mn^{2+} ion.¹² Furthermore, in later studies of Mn-doped semiconductor NCs, Godlewski *et al.* suggested that the observed fast decay

is related to a very efficient spin-flip interaction between the localized spins of Mn^{2+} ions and the spins of free carriers.^{13,14} Chen *et al.* showed that the short component of the radiative lifetime is due to a mixture of donor-acceptor-tail emission and a fast decay emission peaked at 645 nm.¹⁵ The conflicting results from these previous experiments indicate that the decay dynamics of the Mn^{2+} ion embedded in II-VI semiconductor NCs is still an unresolved issue. One possibility is that the reported shortening of radiative lifetime of Mn^{2+} ions in ZnS NCs down to the nanosecond time scale by Bhargava *et al.*⁶ does not reflect the true decay lifetime of Mn^{2+} in ZnS NCs; instead it comes from the residual emissions at the measurement wavelength (near 580 nm) from other nearby emission peaks. However, since the Mn:ZnS NCs synthesized previously have large nearby emission peaks which have significant overlaps at the Mn^{2+} emission wavelength (~ 580 nm), it was difficult to separate the exact contributions from these different emission peaks.

In the current work, we report experimental measurements of radiative lifetimes of Mn-doped ZnSe (Mn:ZnSe) quantum dots (*d*-dots) synthesized recently by the nucleation-doping method.¹⁻³ One important advantage of using such Mn:ZnSe *d*-dots for lifetime measurements is the suppression of the host emission (as well as other emission peaks at nearby wavelengths). As reported earlier, the quantum yield of such Mn-doped ZnSe *d*-dots can reach 50% with very little emission peaks from the ZnSe host NCs (near 420 nm) and other wavelengths (near 640 nm). As a result, emission from the Mn^{2+} ions in the ZnSe crystal field can be well isolated. The recently developed high quality Mn:ZnSe *d*-dots have some advantages over the undoped CdSe quantum dots (which suffer from intrinsic toxicity of cadmium, strong self-quenching caused by their small ensemble Stokes shift,^{16,17} and sensitivities to thermal, chemical, and photochemical disturbances^{1,18,19}) for technical applications. Mn:ZnSe *d*-dots have a valence bandedge at higher energy with respect to ZnS,²⁰ and therefore has a better potential for optoelectronic applications, such as light-emitting diode (LEDs),²¹ lasers,¹⁶ and solid-state lighting.¹⁷

So far, the radiative lifetime has not been measured in such high quality Mn:ZnSe *d*-dots synthesized by nucleation doping. We measured the radiative lifetime at 580 nm, cor-

^{a)}Electronic mail: mxiao@uark.edu.

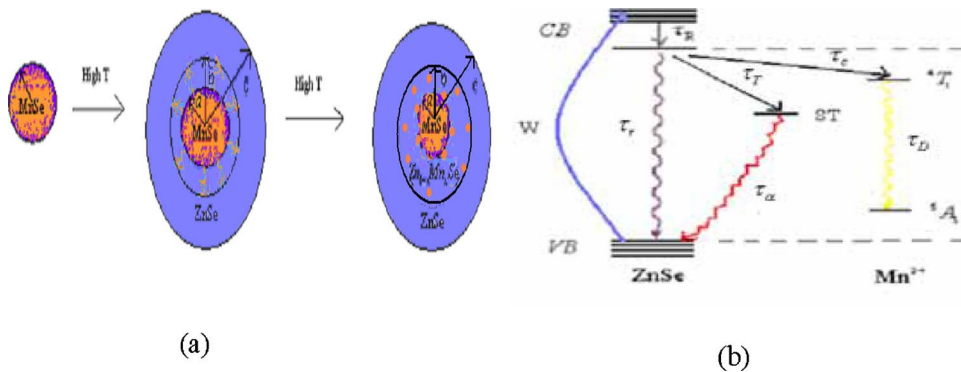


FIG. 1. (Color online) (a) Theoretical structure model for Mn-doped ZnSe *d*-dots via nucleation-doping technique. The MnSe core is 1.5 nm in diameter. There is a diffusion layer with $Zn_{1-x}Mn_xSe$ between radius b and the MnSe core radius a . The amount of Mn ion diffusion depends on the temperature T in synthesis and NC size (bigger NC needs longer synthesis time at temperature T). (b) The relevant energy levels of Mn^{2+} ions embedded in the ZnSe NC.

responding to the luminescent decay from the 4T_1 metastable excited state to the ground state 6A_1 of Mn^{2+} ions. For each NC size, we identified three lifetime components: one dominant slow decay (in the millisecond time scale) corresponding to the decay of Mn^{2+} ions in the ZnSe crystal field and two fast decay components (one with a few nanoseconds and another about 100 ns) corresponding to the decay processes of ZnSe NC host (a few nanoseconds) and, possibly, emission from surface trap states or self-activated emission of Mn^{2+} ion pairs (~ 100 ns), respectively.

The Mn-doped ZnSe *d*-dots were synthesized by nucleation-doping method.¹⁻³ Different size samples have been prepared, with the NC diameters of 3.5, 5.0, and 7.0 nm, respectively. All *d*-dots have the same MnSe core of 1.5 nm in diameter and different ZnSe overcoating layer thicknesses. An amount of Mn^{2+} ions will diffuse into the ZnSe layer during the synthesis process, forming a diffusion region as shown in Fig. 1(a). The diffusion region is a little thicker for the larger NCs following the ion diffusion model.^{22,23} The overall numbers of Mn^{2+} ions are the same for these Mn:ZnSe *d*-dots with different diameters. The energy level diagram of such Mn-doped ZnSe *d*-dots is shown in Fig. 1(b). The valence band and conduction band are for the host ZnSe NCs, which has a surface trap state as in most of colloid NCs.²⁴ After photoexcitation of the host NCs, the population can be very efficiently transferred to the excited metastable state 4T_1 of the Mn^{2+} ions via a fast nonradiative decay. The transition 4T_1 - 6A_1 for the Mn^{2+} ions is near 580 nm (tunable between 575 and 595 nm in the ZnSe host crystal field).² With the nucleation-doping procedure, this Mn^{2+} ion emission is dominant as shown in the measured photoluminescence (PL) spectra for different size Mn:ZnSe *d*-dots [Fig. 2(a)].¹⁻³ There is a weak emission peak near 420–440 nm corresponding to the ZnSe NC host emission. Comparing to the previously made Mn:ZnSe NCs,⁶⁻⁸ this host emission peak is greatly suppressed in our samples.

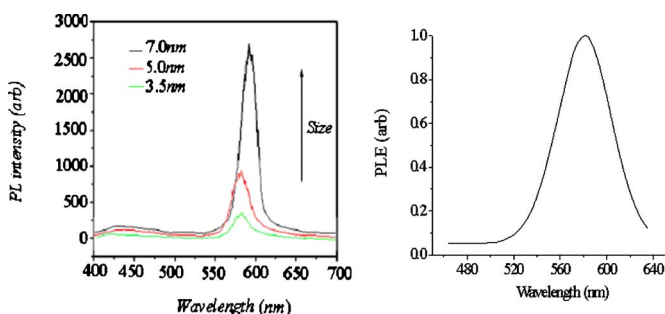


FIG. 2. (Color online) PL spectra for Mn-doped ZnSe NCs with different sizes; (b) PLE spectrum of Mn-doped ZnSe NCs (6 nm diameter).

Also, there is a shoulder at the longer wavelength region (near 640 nm), which could be caused by weak emission via surface trap state or self-activated emission due to ion pairs. This peak is usually much stronger in bulk Mn:ZnSe crystal.^{5,25} PL excitation (PLE) measurement was made near the wavelength region and is shown on Fig. 2(b), which only shows the dominant peak near 580 nm.

The lifetime measurements were carried out for both slow (millisecond) and fast (nanosecond) time scales, using different techniques. To measure the slow lifetime component, we used an optical chopper and a digital oscilloscope to record the PL decay curve. The excitation source is a Ti:sapphire laser operated at picosecond mode with a repetition rate of 82 MHz and is frequency doubled to the wavelength of 400 nm. The PL signal is detected by a photomultiplier. The fast PL decay components were measured by using a time-correlation single-photon-counting system.^{26,27} An electro-optical pulse picker lowered the repetition rate down to 16 MHz. A 0.5 m spectrometer was used to select detection wavelength at 580 nm. The PL signal with the fast decay times is very weak and a much longer photon-counting time had to be used. All measurements were done at room temperature.

The measured slow PL decay curve for the Mn:ZnSe *d*-dots with diameter of 3.5 nm is presented in Fig. 3(a). This curve is a single exponential over two orders of magnitude and is determined to be 0.3 ms. PL lifetimes of other samples of Mn:ZnSe *d*-dots with different sizes are plotted on Fig. 4(a). One can easily see that Mn^{2+} ion emission in the ZnSe crystal field has a longer lifetime for NCs with thicker ZnSe overcoating layer (larger NCs) or thicker diffusing region. Such behavior can be qualitatively understood by the calculated radiative lifetime of an ion embedded in a medium,²⁸

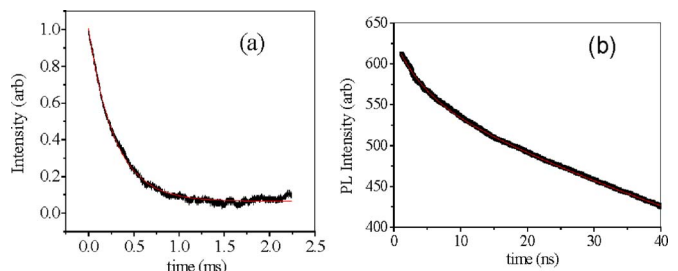


FIG. 3. (Color online) Measured PL decay curves at wavelength near 580 nm by using (a) an optical chopper and oscilloscope giving the slow time decay component in the millisecond time scale; (b) time-correlation photoluminescence system measuring fast decay time components in nanosecond and hundred nanosecond time scales. The PL intensity measured in (b) is much weaker than in (a).

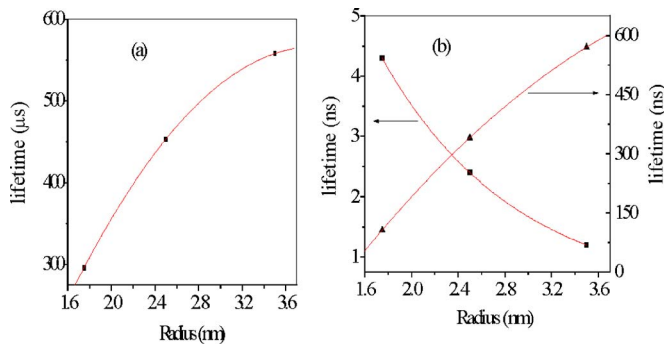


FIG. 4. (Color online) Measured radiative lifetime components near 580 nm for different size Mn-doped ZnSe *d*-dots. (a) The slow decay component from Mn^{2+} ions in ZnSe crystal field; (b) the fast decay components due to the ZnSe host emission at 420 nm (square dot curve) and due to host trap states or self-activated emission of ion pairs at longer wavelength (~ 640 nm) (triangle dot curve).

$$\tau_R \sim \frac{1}{f(\text{ED})} \frac{\lambda_0^2}{\left[\frac{1}{3}(n_{\text{eff}}^2(x) + 2)\right]^2 n_{\text{eff}}(x)}, \quad (1)$$

$$n_{\text{eff}}(x) = xn_{\text{ZnSe}} + (1-x)n_{\text{toluene}}, \quad (2)$$

$$n_{\text{ZnSe}} = \{1 + (\epsilon_{\text{bulk}} - 1)/[1 + (0.75 \text{ nm}/d)^{1.2}]\}^{1/2}, \quad (3)$$

where $f(\text{ED})$ is the oscillator strength for the electric dipole transition, λ_0 is the wavelength in vacuum, and n is the refractive index. x is the “filling factor” showing what fraction of space is occupied by the ZnSe NCs. $\epsilon_{\text{bulk}} \sim 6.0$ is the dielectric constant of bulk ZnSe and d is the average diameter of ZnSe NCs in nanometer. As the NC size increases with the same NC density, the filling factor will be larger, which gives a larger decay lifetime for the embedded ions in the NC. This is consistent with our experimentally measured result [Fig. 4(a)]. So we can conclude that the bigger the size of the Mn-doped ZnSe *d*-dots is, the longer the radiative lifetime from the ${}^4T_1-{}^6A_1$ transition for the Mn^{2+} ions will be.

Using the time-correlation technique, the faster PL decay components of the Mn:ZnSe *d*-dots can be detected, as showed in Fig. 3(b). This PL decay curve for Mn:ZnSe *d*-dots of 3.5 nm was measured at 580 nm wavelength and very weak in intensity. It is a biexponential and can be fitted with two decay time constants; one is in a few nanosecond time scale and another in hundreds of nanosecond time scale. Such curves for the three samples of different sizes were measured and the decay constants are presented in Fig. 4(b). The shortest decay time component shows a decrease as NC size increases, while the longer decay time component shows an opposite trend. The few nanosecond decay time constant is consistent with the primary decay process of the host ZnSe NCs if we consider these Mn-doped ZnSe *d*-dots by nucleation doping a spherical quantum-well structure.²⁹ As previously demonstrated in spherical CdS/CdSe/CdS quantum wells, radiative lifetime decreases as the well thickness increases at room temperature,³⁰ consistent with the result shown in Fig. 4(b). This behavior is different from typical core/shell quantum dots.³¹ For the relatively large PL decay constant (\sim hundreds of nanoseconds) measured in our experiment, it is more consistent with the result reported by

Chen *et al.*,¹⁵ which has been attributed as from the tail of the emission peak at ~ 645 nm wavelength from the Mn-doped ZnSe *d*-dots due to either the surface traps or self-activated emission from ion pairs, as in the bulk crystal.⁵

Resolving the mechanisms of radiative lifetimes in the Mn-doped ZnSe *d*-dots, especially their size dependences, can be very important for the applications of such *d*-dots in biological labeling,³ LEDs,²¹ and lasers.¹⁶

We acknowledge funding supports from the Army Research Office (W911NF-05-1-0353), NSF/MRSEC (DMR-0520550), and Arkansas Science & Technology Authority.

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