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Facile Synthesis of Highly Luminescent Mn-Doped ZnS Nanocrystals

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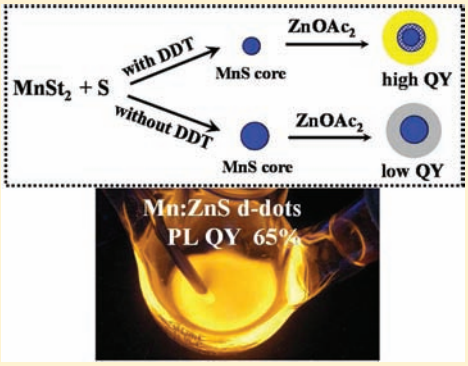

ABSTRACT: Manganese-doped zinc sulfide quantum dots (Mn:ZnS d-dots) with high optical quality, pure dopant emission of 55−65% photoluminescence quantum yield, were synthesized in octadecene media with generic starting materials, namely, zinc (manganese) carboxylic acid salts, S powder, and dodecanethiol (DDT) based on a "nucleation doping" strategy. The optical properties and structure of the obtained Mn:ZnS d-dots have been characterized by UV−vis, photoluminescence (PL) spectroscopy, transmission electron microscopy (TEM), and X-ray diffraction (XRD). The resulting nearly monodisperse d-dots were found to be of spherical shape with a zinc-blende crystal structure. The influences of various experimental variables, including the reaction temperature for the MnS core nanocluster and ZnS host material, the amount of octadecene (ODE)-S, DDT, as well as Zn/Mn ratio have been systematically investigated. The use of DDT as capping ligand ensured the reproducible access to a stable small-sized MnS core. This paves the way for reproducibly obtaining highly luminescent d-dots. Programmed overcoating temperature for growth of ZnS shell was employed to realize balanced diffusion of the Mn ions in the d-dots.

INTRODUCTION

The critical role that dopants play in semiconductor devices has stimulated research on the properties and the potential applications of doped semiconductor nanocrystals (NCs), also named doped quantum dots (d-dots). Colloidal d-dots have drawn considerable attention in recent years because of their unique optical, electronic, and magnetoptical properties and consequently in potential applications as optoelectronic devices and biomedical tags and so forth.[1−5] Currently, a variety of synthetic approaches have been developed for transition metal ions (mainly Mn^{2+}) doped zinc chalcogenides (including ZnSe and ZnS) NCs,[6−30] in which the transition metal ligand-field excited states reside within the bandgap of the host semiconductor. Such materials have been shown to display nearly pure and efficient sensitized dopant photoluminescence (PL). As an emitter, these d-dots could not only replace CdSe or CdTe quantum dots with nontoxic or low-toxic 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, and sensitivity to thermal, chemical, and photochemical disturbances.[31−34]

Because of the potential high photoluminescence quantum yields (PL QYs) from the Mn^{2+} $^4T_1$−$^6A_1$ transition and suitable valence band edge of the host for application in electroluminescent devices, the Mn:ZnS,[6−16] and Mn:ZnSe[17−30] d-dots have attracted extensive attention. There has been a sustained effort for more than a decade to enhance the dopant emission from doped NCs. In the early stage, most reports on d-dots used a colloidal route based on the simultaneous precipitation of both host materials and dopants.[6−9,17,18] All these studies have concluded that only a small fraction of the initial manganese used is incorporated into the crystal lattice with a large proportion of the manganese remaining on the surface. This situation was substantially improved by Peng's group with the development of a new doping strategy by decoupling the doping from nucleation and/or growth through nucleation-doping and growth-doping approaches.[21−24] Nucleation doping was realized by a mixed dopant and host precursor during the nucleation. In an extreme case, the nuclei could be formed with pure dopant cations and followed by the growth of a host shell on the core. Under the nucleation-doping strategy, MnSe nuclei were overcoated with ZnSe shell. No residual ZnSe emission was observed, and the doped NCs exhibited thermally stable highly efficient PL with QY of 40−70%.[21−24] For Mn:ZnS d-dots, they are a greener material that is free from both Cd and Se, and popular nanophosphors for electroluminescent devices.[35,36] In comparison, the synthesis of Mn:ZnS is not as advanced, and few examples have been given for the synthesis of high quality Mn:ZnS d-dots by the nucleation- or growth-doping strategy. Recently, high quality Mn:ZnS d-dots or doped nanorods with PL QY around 35−50% have been prepared via the nucleation- or growth-doping strategy.[13−16]

Herein, we report the preparation of highly luminescent Mn:ZnS d-dots with use of DDT as a capping ligand under the nucleation-doping strategy in octadecene media. Alkyl thiols are soft Lewis base ligands for transition metal ions and thus can form stable metal complexes to lower the reactivity of metal ions precursors. Therefore, the DDT ligand can make Mn much less reactive, and thus lead to form stable small-sized MnS core

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nanoclusters. The synthesis is based on a two-step approach: (i) synthesis of small-sized MnS core nanoclusters, (ii) overcoating ZnS shell around MnS core accompanied with the Mn dopant diffusion and formation of Mn ions diffusion layer between the MnS core and ZnS shell. We found that the use of DDT as capping ligand ensured the reproducible access of stable small-sized MnS core nanoclusters, and the programmed overcoating temperature for ZnS host material growth realized the balanced diffusion of Mn ions in the d-dots.

EXPERIMENTAL SECTION

Chemicals. Zinc acetate ($Zn(OAc)_2$, 99.99%), manganese chloride ($MnCl_2$, 99.99%), zinc diethyldithiocarbamate (ZDC, 98%), 1-dodecanethiol (DDT, 99.9%), tetramethylammonium hydroxide pentahydrate (TMAH), sulfur powder (99.99%), 1-octadecene (ODE, 90%), stearic acid (SA, 95%), and oleylamine (OAm, 70%) were purchased from Aldrich. All chemicals were used as received without any further purification.

Preparation of $MnSt_2$ and Zinc Stock Solution. The manganese precursor, manganese stearate ($MnSt_2$), was prepared according to a literature method.[22] Typically, SA (20 mmol) was dissolved in 35 mL of methanol with the aid of heating to get a clear solution. A solution of TMAH (obtained by dissolving 20 mmol of TMAH in 15 mL of methanol) was mixed with the SA solution. To this solution, 10 mmol of $MnCl_2$ dissolved in 15 mL of methanol was added dropwise with vigorous stirring, and a white precipitate of $MnSt_2$ slowly flocculated. The precipitates were repeatedly washed with methanol and dried under vacuum.

The zinc stock solution (0.5 M) for ZnS shell growth was prepared by dissolving 2.195 g (10 mmol) of $Zn(OAc)_2$ in a mixed solvent system containing 6.0 mL of OAm and 14.0 mL of ODE at 160 °C under nitrogen flow. The obtained Zn stock solution was stored at 50 °C for the following use.

Synthesis of Mn:ZnS d-Dots through Nucleation-Doping Strategy. Typically, 0.1 mmol (62.2 mg) of $MnSt_2$, 1.0 mL of DDT, and 3.0 mL of ODE were loaded into a 50 mL three-neck flask and degassed at 100 °C for 15 min under vacuum. Then the reaction system was filled with N_2, and the temperature was further raised to 250 °C to get a colorless and clear solution. At this temperature, 0.5 mL of sulfur solution in ODE (0.4 M), obtained by dissolving sulfur powder in ODE at 120 °C, was injected into the reaction system. Immediately after the injection of sulfur solution, the color of the reaction solution turned to faint yellow, showing the formation of MnS nanoclusters. Two min after the injection of sulfur solution, Zn stock solution was added dropwise to the vigorously stirred solution via a syringe pump in a period of 2−3 h. Immediately after the addition of Zn precursor to the S-rich system, the solution color became golden yellow. To monitor the reaction, periodically small aliquots were taken for measuring UV−vis and PL spectra. When 1 mL of Zn stock solution was added into the reaction system, reaction temperature was lowered down to 230 °C for the further overgrowth of ZnS shell with addition of another 1 mL of Zn stock solution. After finishing the addition of stock solution, the reaction mixture stayed at 230 °C for another 20 min to ensure the complete consumption of the Zn precursor. Finally, the reaction was cooled down to room temperature, and the NCs were purified using methanol/hexane extraction with the d-dots in the hexanes layer. This procedure can reproducibly prepare Mn:ZnS d-dots with PL QY in the range of 55−65%.

Characterization. UV−vis and PL spectra were obtained on a Shimadzu UV-2450 spectrophotometer and a Cary Eclipse (Varian) fluorescence spectrophotometer, respectively. The room-temperature PL QY of the QDs were determined by comparing the integrated emission of the QDs samples in solution with that of a fluorescent dye (such as rhodamine 6G with a QY of 95% in ethanol) with an identical optical density.[37,38] Also, the known QYs of the QDs in solution can be used to measure the PL efficiencies of other QDs by comparing their integrated emission. To conduct investigations with the transmission electron microscopy (TEM), the NCs were deposited from dilute toluene solutions onto copper grids with carbon support by slowly evaporating the solvent in air at room temperature. TEM images were acquired using a JEOL JEM-1400 transmission electron microscope operating at an acceleration voltage of 120 kV. Powder X-ray diffraction (XRD) was obtained by wide-angle X-ray scattering using a Siemens D5005 X-ray powder diffractometer equipped with graphite monochromatized Cu Kα radiation (λ = 1.5406 Å). XRD samples were prepared by depositing NC powder on a piece of Si (100) wafer.

RESULT AND DISCUSSION

Formation of Small-Sized MnS Core Clusters. Herein, a nucleation doping strategy was adopted for the preparation of Mn:ZnS d-dots. In the first step, small sized MnS core NCs were synthesized based on a hot-injection of S precursor ODE-S into the noncoordinating solvent ODE system containing Mn precursor ($MnSt_2$) and DDT at 250 °C. A ZnS shell was then overcoated around the MnS cores with the introduction of $Zn(OAc)_2$ into the "S"-rich system containing the preformed small-sized MnS core nanocluster. The resulting NCs can be considered as a MnS/ZnS core/shell or MnS/Mn:ZnS/ZnS quantum well structure from the structural viewpoint. For simplicity, these NCs are called d-dots as done in previous reports because of their similar emission properties.[13,14,21−24]

It is well-known that the emission features of dopant Mn^{2+} ions in d-dots are closely related to the distribution of Mn^{2+} ions in the d-dots and the structure of the d-dots.[13,14,21−24] For the case of MnS/Mn:ZnS/ZnS quantum well structures, the PL of dopant Mn ions is currently considered to come from the energy transfer from photoexcited ZnS shells to the Mn ions in a diffusion layer at the interface between the MnS core and the pure ZnS overcoating layer. High PL QY of dopant Mn ions in Mn:ZnS d-dots could be obtained by controlling the formation of the Mn ions diffusion layer at the interface between the MnS core and the ZnS outer layer. Accordingly, control of the size of the MnS cores is the first key issue in this nucleation-doping strategy to obtain highly luminescent dopant emission in Mn:ZnS d-dots. Ideally, a small-sized core cluster would place the dopant ions as close as possible to the center of the d-dots. This shall result in emission centers as far away as possible from the potential surface trap states of the NCs, and thus improve the optical performance of the d-dots. A small core cluster also means a relatively uniform environment of the doping ions in a d-dot. Furthermore, a small-sized core might be more suited for formation of a high-quality diffusion layer at the interface between the MnS core and the ZnS shell in comparison to a large-sized MnS core because of the stronger quantum confinement effect.[39] Therefore, we chose advisable reaction condition with use of DDT as capping ligand to obtain small sized MnS core nanoclusters.

In recent years, alkyl amines have been used predominantly as capping ligand for synthesis of Mn doped zinc chalcogenides NCs.[13−15,21−24] When manganese carboxylates were used as Mn precursor, however, tuning the fine size of MnS nucleus was found to be difficult when the solution was composed of pure noncoordinating solvent (such as ODE), alkyl amines, carboxylic acid, and their mixtures. In the case of the Mn:ZnSe system, one simple way to suppress the formation of large-sized MnSe core NCs via continuous growth is to add large excess amounts of the anionic precursor.[21−24] In previous report for the synthesis of Mn:ZnSe d-dots,[24] when the Mn to Se precursor was up to 1:25, small sized (less 2 nm) MnSe core NCs can be obtained with long-term stability at a growth temperature of 250 °C. In contrast, in the preparation of metal sulfide NCs, use of large excess of S precursor is not valid for the formation of small sized MnS core NCs. In previous reports,[13,14] the resulting MnS core NCs is about 2.3 nm even terminating the reaction right after the mixing of Mn and S precursors at high temperature.

To control the growth of NCs, selecting capping ligand is a key issue, because a kind of appropriate ligand can commendably limit growth of NCs to form smaller NCs cores. The coordination ability of the mercapto group is stronger than phosphorus, oxygenous, nitrogenous groups and renders a strong binding capacity with the surface atoms of the NCs. Therefore, the thiol ligands can make Mn much less reactive, and thus lead to form stable small-sized MnS core nanoclusters. In previous reports,[40−42] thiols were successfully used as ligands for formation of high-quality I−III−VI semiconductor NCs by balancing the reactivity of two cationic precursors. For this reason, we chose DDT as capping ligand to obtain stable small sized MnS core NCs under the nucleation doping strategy for Mn:ZnS d-dots.

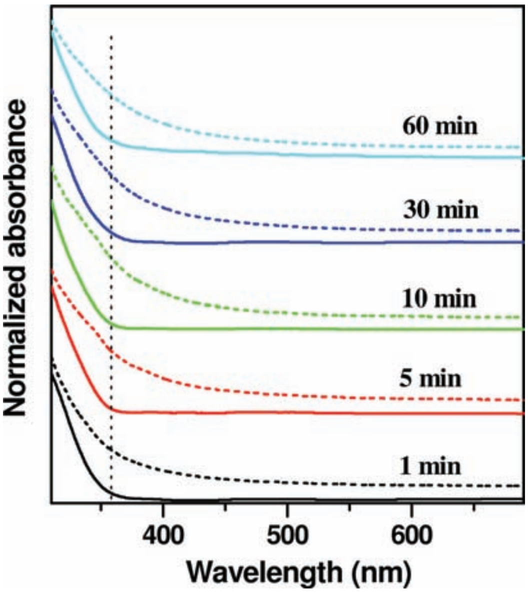

Figure 1. Temporal evolution of UV−vis absorption spectra of MnS nanoclusters synthesized with (solid curves) and without (dotted curves) the use of DDT ligand.

The effect of using DDT in controlling the size of the formed MnS core is distinctive. When DDT was chosen as capping ligand in the preparation of MnS core NCs with the use of manganese stearate and ODE-S as corresponding Mn/S precursors, the absorption edge of the MnS clusters stayed around 360 nm with a corresponding particle size smaller than 2 nm even after the heating time was up to 1 h (solid curves in Figure 1); while in the control experiment without the presence of thiol ligands, the formed MnS nanocluster can grow larger sharply via continuous growth and lead to less reproducibility of the synthetic method (dotted curves in Figure 1). The access of stable small sized MnS core nanoclusters with the use of DDT as capping ligand paves the way for preparation of highly luminescent Mn:ZnS d-dots reproducibly. It was found that when we repeated our synthetic approach 10 times, the PL QYs of the obtained Mn:ZnS d-dots could be in the range of 55−65%.

Optical Properties of Mn:ZnS d-Dots. As shown in Figure 2A, the UV−vis absorption spectra of Mn:ZnS d-dot samples show the characteristics of a quantum well structure without the distinguished absorption onset,[22] and the featureless absorption at the UV region should be related to the absorption of the ZnS host. A strong PL band is observed at about 587 nm, which is ascribed to the Mn^{2+} ion $^4T_1$−$^6A_1$ transition.[43,44] The highest PL QY of 65% can be obtained when the nominal Zn/Mn ratio is 10:1, and the corresponding photograph of the emission color is shown in the inset of Figure 2A. Compared with that of previously reported Mn:ZnS d-dots,[6−10] the trap state emission, appearing near 400−500 nm, is greatly suppressed in our samples, implying preparation of the high-quality Mn-doped QDs.

It was found that the Mn ion dopant PL intensity increased rapidly with increase of ZnS shell thickness as shown in Figure 2B. With the overgrowth of ZnS shell around the preformed MnS core nanoclusters, faint Mn PL was observed. When the nominal Zn/Mn ratio was less than 5 (i.e, the ZnS shell around MnS is thin), the PL intensity of the resulting MnS/ZnS was relative low (PL QY is less than 10%). When the Zn/Mn ratio was greater than 5:1, with the increasing of ZnS shell thickness the PL QYs of the resulting Mn:ZnS increased sharply and approached the highest value of 65% when the Zn/Mn ratio

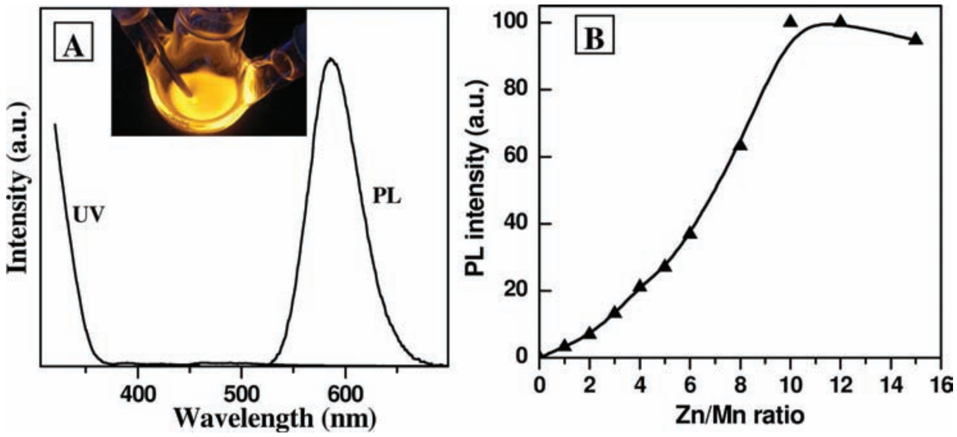

Figure 2. (A) Typical UV−vis absorption and PL (λ_{ex} = 300 nm) emission spectra of Mn:ZnS d-dots. (Inset) Digital photograph of Mn:ZnS d-dots under irradiation of a UV lamp. (B) The dependence of PL intensity of Mn:ZnS d-dots on the nominal Zn/Mn ratio.

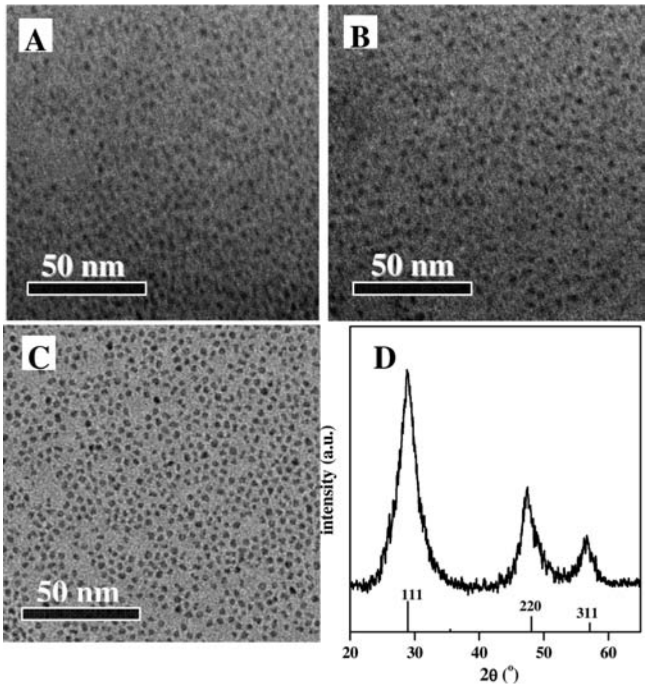

Figure 3. TEM images of Mn:ZnS d-dots with Mn/Zn precursor ratios of (A) 1:1.2, (B) 1:5, and (C), 1:10. (D) Typical XRD patterns of the Mn:ZnS d-dots with Mn/Zn precursor ratios of 1:10. The line spectrum (bottom) indicated the reflections of zinc blende bulk ZnS.

was 10:1. With further increase of the ZnS thickness, the PL QY decreased gradually. This observed dependence of the PL intensity of the Mn:ZnS d-dots on Zn/Mn ratio can be explained by the Mn dopant PL mechanism. The PL of Mn ions comes from the energy transfer from photoexcited ZnS shells to the Mn ions in a Mn ion diffusion layer located between the MnS core and the pure ZnS overcoating layer.[22] For the Mn:ZnS d-dots synthesized by the nucleation doping strategy, the formation of the diffusion layer was considered to derive from the diffusion from the MnS core into the ZnS shell during the growth process. When the Zn/Mn precursor ratios were low (less than 5:1), that is, the ZnS shell is thin, Mn^{2+} ion emission centers are closer to the surface of the d-dots, where a higher possibility exists to quench the Mn PL by surface traps, so a weak Mn ion PL band is observed. With overcoating the ZnS shell, the Mn ion diffusion layer is deeper placed in the d-dots, and a strong PL band is thus observed.

Morphology and Structure. TEM was used to monitor and characterize the overall size of the obtained d-dots, and the thickness of the shell can be calculated correspondingly. The size of the obtained MnS nanoclusters under the experimental condition was too small to be detected using TEM. Figure 3 shows the TEM images of the corresponding Mn:ZnS d-dots with nominal Mn/Zn precursor ratios of 1:2, 1:5, and 1:10. The corresponding average diameters of the d-dots were determined to be 2.9 ± 0.3, 3.6 ± 0.3, and 4.5 ± 0.4 nm, respectively. TEM images demonstrate that all of the as-obtained NCs are of near-spherical shape and possess high size uniformity. Taking the MnS core diameter of 2.0 nm and the thickness of ZnS monolayer as 0.32 nm, the ZnS shell layer correspond to 1.4, 2.5, and 4 monolayers, respectively.

The wide-angle XRD patterns of the obtained Mn:ZnS d-dots with Mn/Zn precursor ratios of 1:9.6 display the (111), (220), and (311) planes as shown in Figure 3E, meaning that it is cubic (zinc blende) phase (JCPDS card no. 77-2100), which supports the hypothesis that Mn^{2+} is more facile to incorporate in cubic ZnSe NCs than in wurtzite and rock-salt crystals.[19] No diffraction peaks from manganese impurities were detected in the sample. In addition, we can conclude that doping Mn^{2+} into the host NCs does not bring about a phase transformation of the crystal structure.

PL Properties of Mn:ZnS d-Dots Dependent on Synthetic Conditions of MnS Core Nanoclusters. The synthetic conditions of the MnS cores nanoclusters were found to play a critical role in determining the PL properties of the resulting Mn:ZnS d-dots. First, the reaction temperature for the synthesis of the MnS core nanoclusters influences the PL QY of the resulting d-dots greatly. The experimental results revealed that to obtain highly luminescent Mn dopant emission in the Mn:ZnS d-dots, the optimal reaction temperature for introducing the sulfur precursor solution ODE-S into the reaction flask for formation of MnS NCs was 250 °C. If the temperature was too low or too high relative to 250 °C, the PL intensity (normalized to the same absorbance at the excitation wavelength) of the dopant emission in the resulting d-dots was significantly lower than that obtained at 250 °C as shown in Figures 4A and 4B. The PL intensity of the resulting Mn:ZnS d-dots at 210 °C is less than 1/10 of that at 250 °C (Figure 4B). Too low temperature was not adequate for the formation of MnS nanoclusters, while too high temperature would lead to formation of large-sized MnS core NCs and accelerate the decomposition of DDT. These effects would deteriorate the PL QY of the resulting d-dots, since a large sized MnS core NC is not favorable for the Mn diffusion and formation of the diffusion layer because of the weak quantum confinement effect.[39] As shown in Figure 4C, the dopant PL intensity of the resulting d-dots was not sensitive to the reaction time, and high PL QY can be kept with reaction time extending up to 10 min. After that, with further extension of the growth time, it actually started to decrease. This feature of the PL QY not being sensitive to the reaction time can bring a high reproducibility of this synthetic approach to obtain highly luminescent d-dots. If not specified, the d-dots mentioned in this report were all based on such MnS nanoclusters formed at 250 °C for about 2 min.

Influence of Amount of ODES. A stable and small-sized MnS core nanocluster is a prerequisite for high-quality Mn:ZnS d-dots under the nucleation-doping strategy. Because of the strong coordination ability of DDT to free metal ions and surface atoms of MnS NCs, DDT can favorably limit the growth of NCs to obtain small-sized MnS core nanoclusters. On one hand, DDT acts as a kind of appropriate ligand, on the other hand it can simultaneously support a sulfur source after thermal decomposition during the reaction. Consequently, we tried to use DDT alone as a sulfur source to prepare Mn:ZnS d-dots. The experimental results revealed that with the use of DDT alone as sulfur source, the PL QY of the resulting d-dots was very low. If the amount of DDT was greater than 2 mL, a yellow precipitation was formed within the reaction mixture. Therefore, DDT acting as sole sulfur source should not be suitable for obtaining high-quality Mn:ZnS d-dots, and the optimal amount of DDT was chosen as 1.0 mL.

The fact that DDT cannot serve as the sole sulfur source for the preparation of high-quality Mn:ZnS d-dots pushed us to use ODE-S as another sulfur source. ODE-S should be one of the best choices to serve as sulfur source, since it has high reactivity to metal ions and is air-stable and thus conveniently processable. In

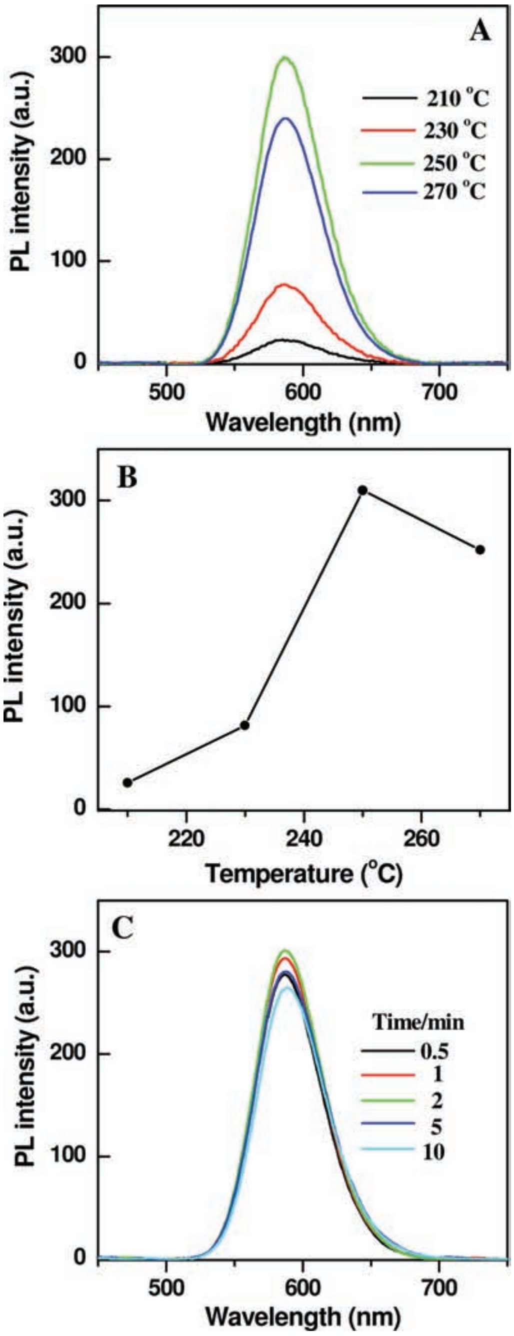

Figure 4. PL spectra (A) and relative PL intensity (B) of Mn:ZnS d-dots depending on the reaction temperature for synthesizing MnS core nanoclusters, and (C) PL spectra of Mn:ZnS d-dots depending on the reaction time of MnS core nanocluster growing at 250 °C.

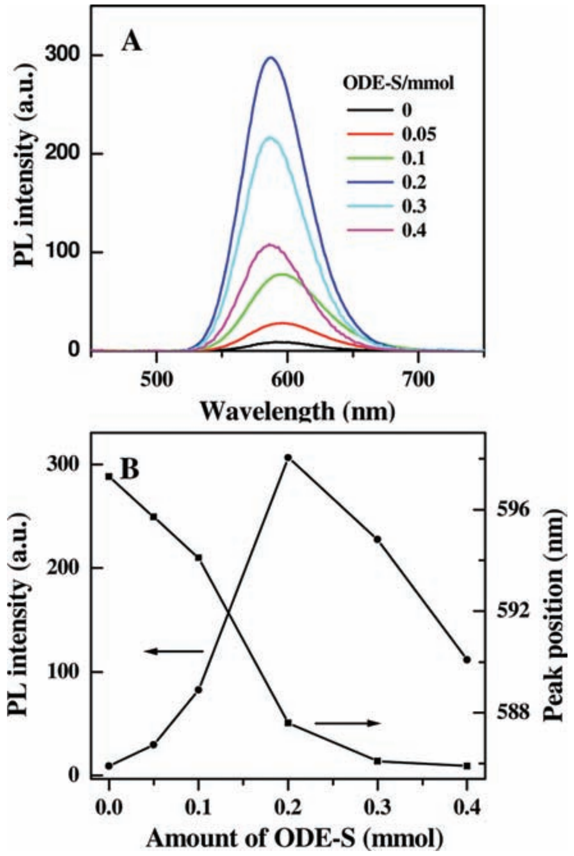

Figure 5. (A) PL spectra of Mn:ZnS d-dots dependent on the amount of ODE-S, and (B) summary of PL peak intensity and peak position dependent on the amount of ODE-S.

the following experiment, we investigated the optimal amount of ODE-S with the fixation of other reaction variables as stated in the Experimental Section. Figure 5A shows that the PL intensity of the resulting Mn:ZnS d-dots is heavily dependent on the amount of ODE-S used, and the corresponding PL intensity and peak position are summarized in Figure 5B. In principle, with increase of the ODE-S amount, the Mn ion PL intensity increased rapidly and approached the highest intensity at ODE-S of 0.2 mmol. Simultaneously, with increase of the ODE-S amount the PL peak position blue-shifted monotonically from 594 to 587 nm. With the increase of ODE-S, the cationic precursor, Mn fatty acid salts should be consumed rapidly. This is favored for formation of small-sized MnS nanoclusters, and the formed small MnS nanoclusters should be stable in the reaction solution because of the existence of an excessively high concentration of sulfur monomer in the solution. As described above the formation of small-sized MnS core nanoclusters is the prerequisite for obtaining highly luminescent dopant emission in the Mn:ZnS d-dots. However, the Mn ion emission reduced systematically when the amount of ODE-S was higher than 0.2 mmol. The presence of excess amount of ODE-S may result in the S-rich surface of the obtained Mn:ZnS d-dots. The formation of dangling bonds of the S^{2-} species would cause the PL emission to deteriorate and thus brings about the decrease of PL intensity.

Influence of Overcoating Temperature of ZnS Shell. Effective "dopant diffusion" during overcoating of host material is critical for obtaining high-quality dopant PL in d-dots via the nucleation doping strategy. Undoubtedly, the overcoating temperature (T_{oc}) for ZnS host material growth is one of the most important factors in determining the dopant diffusion process, and thus T_{oc} has a significant influence on the optical properties of resulting Mn:ZnS d-dots. As show in Figure 6, with the same type of MnS nanoclusters cores, at a relatively low T_{oc} of 210 °C, dopant Mn^{2+} PL emission can be observed only after the Zn precursor stock solution was added up to a Zn/Mn ratio of 3:1; after that the PL intensity increased continuously but slowly within the experimental ZnS layer frame. On the other hand, when the T_{oc} was set at 250 °C, with the introduction of the first

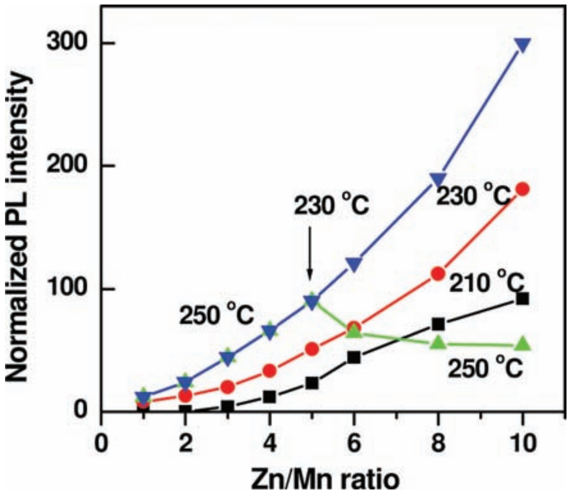

Figure 6. Normalized PL intensity of Mn:ZnS d-dots dependent on ZnS shell overcoating temperature.

batch of Zn stock solution, the color of the reaction solution turned to golden yellow instantly, which indicated the fast growth of the ZnS shell. The PL intensity increased fast and reach a sharp maximum at about a Zn/Mn ratio of 5:1; following that the PL intensity decreased fast. When the T_{oc} was set at 230 °C, the intensity of the dopant PL increased steadily and reached the highest value at a Zn/Mn ratio of 10:1. With further introduction of Zn stock solution, the color of the reaction mixture changed to orange slowly from the initial yellow, and the solution turned to turbid gradually accompanied with the reduction of PL intensity. However, the PL QY did not reach very high (<30%) under a T_{oc} of 230 °C. In our procedure for overcoating ZnS host materials, a programmed overcoating temperature was adopted at different shell growth stages as shown in Figure 6. In the first stage, higher temperature (250 °C) was adopted before the Zn/Mn ratio approached 1:5; then the temperature was lowered to 230 °C for continuous overgrowth of the ZnS shell. Experimental results revealed that higher PL QY can be obtained with use of a two stage temperature than a single temperature (230 °C or 250 °C).

The influence of T_{oc} on the dopant PL emission of the resulting d-dots is mainly derived from the influence on the dopant Mn ion diffusion. If T_{oc} is too low (such as 210 °C) to spur the diffusion of Mn ions, dopant Mn ions were retained mostly within the interior lattice of the core nanoclusters, and an effective diffusion layer could not formed; and thus the structure behaved like a core/shell structure with MnS core and ZnS shell layer. In this case no effective energy transfer from host materials to dopant ions and thus poor PL properties would be observed. In contrast, when the T_{oc} is too high, a large amount of dopant Mn ions undergo a diffusion process. A high concentration of dopant ions were placed right next to each other within the center of the d-dots, and the strong Mn−Mn interaction is not favored for the high PL.[8,32,45] In another extreme case, Mn ions migrated to the surface of the d-dots or even ejected out of the d-dots. This will result in the increase of the nonradiative relaxation rate from the Mn ions to the quenching center, thus quenching PL. The advantage of overgrowth of the ZnS shell under two temperature stages could be explained by controlled diffusion. In the beginning stage, higher temperature benefits the diffusion of Mn ions to form the diffusion layer around the thin shell of d-dots. With the formation of the diffusion layer, further diffusion of Mn ions is not necessary; then a lower growth temperature is only needed for the thickening of the ZnS shell, but the diffusion is stopped. As a result, a continuous growth of the ZnS host lattice would provide an additional passivation layer for the dopant Mn emission center, which can further enhance the PL emission.

■ CONCLUSION

In summary, highly emissive Mn:ZnS d-dots with PL QY in the range of 55−65% were synthesized based on "nucleation-doping" strategy in ODE media. By judiciously choosing DDT as capping ligand, formation of stable small-sized MnS core nanoclusters ensures the reproducible production of high-quality d-dots through the construction of a dopant Mn ions diffusion layer at the interface of the MnS core and ZnS host shell. Programmed overcoating temperatures for ZnS host growth were optimized to control the "lattice-diffusion" of the Mn ions incorporated into the d-dots.

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