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Synthesis of Highly Emissive Mn-Doped ZnSe Nanocrystals without Pyrophoric Reagents

Ruosheng Zeng,[†,‡] Michael Rutherford,[‡] Renguo Xie,[‡] Bingsuo Zou,[†] and Xiaogang Peng*[,‡]

[†] *Micro-Nano Technologies Research Center and Key Lab for Micro-Nano Optoeletronic Devices of Ministry of Education, Hunan University, Changsha 410082, China, and* [‡] *Department of Chemistry and Biochemistry, University of Arkansas, Fayetteville, Arkansas 72701*

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Manganese-doped zinc selenide quantum dots (Mn:ZnSe d-dots) with high optical quality, pure dopant emission with 40−60% photoluminescence quantum yield, were synthesized with air-stable and generic starting materials, namely zinc (manganese) fatty acid salts with corresponding free fatty acids, Se powder, fatty amine, and octadecene. The pyrophoric, highly toxic, and expensive organophospines were eliminated from the existing synthetic protocols for high quality Mn:ZnSe d-dots, which changed the reaction profile substantially mainly because of the enhanced reactivity of elemental Se with the presence of fatty amines. The reaction temperatures for two key processes involved in "nucleation-doping", namely, formation of MnSe nanoclusters and their overcoating by the host, were both reduced. Multiple injection techniques were employed to realize balanced diffusion of the Mn ions in the d-dots. The resulting d-dots were found to be in zinc-blende crystal structure, with optimal spherical shape, nearly monodispersed, and controlled in their Mn:Zn ratio.

Introduction

Semiconductor nanocrystals, or quantum dots (q-dots), with their dimensions below the size of their bulk exciton have been widely explored for their unique fundamental properties and potential application.[1−5] Similar to the situation in the field of modern semiconductor science and technology, doping should play a critical role for semiconductor nanocrystals.[6−15] Recent results revealed that it is possible to dope nearly all nanocrystals in a reaction with a variety of combination of dopants and host materials, which yielded high-quality doped quantum dot (d-dot) emitters with nearly pure and efficient dopant photoluminescence (PL) but not containing any Class A heavy metal ions (Cd, Hg, and Pb).[13,16−18] These highly emissive d-dots are not only as efficient as standard q-dots, such as CdSe-based ones, but also possess some unique properties, which include zero-reabsorption, high temperature stability, and reduced chemical sensitivity. Consequently, in comparison to q-dots, these special properties make these unique emissive materials ideal for solid-state lighting, light-emitting diodes, lasers, and any other applications that may involve significant temperature effects and/or require a high concentration of emitters.[16,19]

Provided the tight environment concerns and tough energy demanding, these "non-Class A metal" d-dot emitters offer a much more attractive future in comparison to the current q-dots workhorse, namely CdSe-based ones. Unfortunately, the existing synthetic chemistry of these "non-Class A metal" d-dot emitters always involves pyrophoric and dangerous chemical reagents. For the most developed d-dots systems, Mn-doped and Cu-doped ZnSe (Mn:ZnSe and Cu:ZnSe) ones,[13,16] organo-phosphines have been used as the ligands for introducing Se precursor—starting as Se powder—into the reaction

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*Corresponding author. E-mail: xpeng@uark.edu.

(1) Brus, L. E. *J. Chem. Phys.* **1984**, *80*(9), 4403–4409.
(2) Weller, H. *Angew. Chem., Int. Ed.* **1993**, *32*(1), 41–53.
(3) Alivisatos, A. P. *J. Phys. Chem.* **1996**, *100*(31), 13226–13239.
(4) Murray, C. B.; Kagan, C. R.; Bawendi, M. G. *Annu. Rev. Mater. Sci.* **2000**, *30*, 545–610.
(5) Peng, X. G. *Nano Res.* **2009**, *2*(6), 425–447.
(6) Bhargava, R. N.; Gallagher, D.; Hong, X.; Nurmikko, A. *Phys. Rev. Lett.* **1994**, *72*(3), 416–419.
(7) Chamarro, M. A.; Voliotis, V.; Grousson, R.; Lavallard, P.; Gacoin, T.; Counio, G.; Boilot, J. P.; Cases, R. *J. Cryst. Growth* **1996**, *159*(1−4), 853–856.
(8) Mikulec, F. V.; Kuno, M.; Bennati, M.; Hall, D. A.; Griffin, R. G.; Bawendi, M. G. *J. Am. Chem. Soc.* **2000**, *122*(11), 2532–2540.
(9) Norris, D. J.; Yao, N.; Charnock, F. T.; Kennedy, T. A. *Nano Lett.* **2001**, *1*(1), 3–7.
(10) Yang, P.; Lu, M. K.; Xu, D.; Yuan, D. L.; Zhou, G. J. *Chem. Phys. Lett.* **2001**, *336*(1−2), 76–80.
(11) Hanif, K. M.; Meulenberg, R. W.; Strouse, G. F. *J. Am. Chem. Soc.* **2002**, *124*(38), 11495–11502.
(12) Radovanovic, P. V.; Norberg, N. S.; McNally, K. E.; Gamelin, D. R. *J. Am. Chem. Soc.* **2002**, *124*(51), 15192–15193.
(13) Pradhan, N.; Goorskey, D.; Thessing, J.; Peng, X. G. *J. Am. Chem. Soc.* **2005**, *127*(50), 17586–17587.
(14) Yang, Y. A.; Chen, O.; Angerhofer, A.; Cao, Y. C. *J. Am. Chem. Soc.* **2006**, *128*(38), 12428–12429.
(15) Norris, D. J.; Efros, A. L.; Erwin, S. C. *Science* **2008**, *319*(5871), 1776–1779.
(16) Pradhan, N.; Battaglia, D. M.; Liu, Y. C.; Peng, X. G. *Nano Lett.* **2007**, *7*, 312–317.
(17) Xie, R. G.; Peng, X. G. *J. Am. Chem. Soc.* **2009**, *131*(30), 10645–10651.
(18) Zheng, J. J.; Yuan, X.; Ikezawa, M.; Jing, P. T.; Liu, X. Y.; Zheng, Z. H.; Kong, X. G.; Zhao, J. L.; Masumoto, Y. *J. Phys. Chem. C* **2009**, *113*(39), 16969–16974.
(19) Wood, V.; Halpert, J. E.; Panzer, M. J.; Bawendi, M. G.; Bulovic, V. *Nano Lett.* **2009**, *9*(6), 2367–2371.

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system. It should be noticed that, except organo-phosphines, the existing synthetic schemes developed for high-performance Mn:ZnSe and Cu:ZnSe d-dots are solely based on air-stable and generic chemicals, including Zinc fatty acid salts, fatty acids, fatty amines, octadecene (ODE), and Se powder. Provided the promising industrial future of these high performance emitters, elimination of pyrophoric, highly toxic, and expensive organo-phosphine should be at least of interest for production and processing at industrial settings.

Given the obvious interests, d-dots have actually been explored for many years, and some promising results were reported in literature.[6−12] Recently, introduction of a concept, "decoupling doping from nucleation and/or growth", made it possible to nearly dope all nanocrystals presumably with controlled radial distribution of the dopants.[13] Mechanisms of this type of doping schemes[13,17,20−22] and more traditional doping approaches[8,15,23,24] have also been actively explored. One goal of this work is to verify some of existing theoretic models and further enrich our knowledge on doping in nanometer size regime.

In the literature, it has been reported that Se powder might be introduced into the synthesis of CdSe nanocrystals by using hydrocarbon solvents under elevated temperatures.[25] In addition, textbook knowledge tells us that the solubility and reactivity of Se powder under basic conditions could be greatly enhanced.[26] These facts encouraged us to explore synthetic schemes of Mn:ZnSe d-dots using nonpyrophoric reagents. During the preparation/review process of this manuscript, we noticed two very recent reports were published on synthesis of ZnSe q-dots and ZnSe based d-dots using nonpyrophoric reagents.[27,28] In this report, our results would demonstrate that, in place of organo-phosphine, fatty amines—already used in the existing synthetic schemes for Mn:ZnSe d-dots[13,16]—could be used as salvation aid and activation reagents for synthesis of high quality Mn:ZnSe d-dots. The resulting d-dots grown by this alternative method were found to be with high optical quality, i.e., pure dopant emission and reproducibly 40−60% PL quantum yield, and with good control of their size and shape.

Experimental Section

Materials. Zinc stearate ($ZnSt_2$), stearic acid (HSt), and selenium powder (200 mesh, 99.999%), oleyl amine ($\geq$70%) were purchased from Aldrich. 1-Octadecene (ODE, 90%) was purchased from Alpha Aesar. Manganese stearate ($MnSt_2$) was purchased from City Chemical. All organic solvents were purchased from EM Sciences. All chemicals were used without further purification.

Preparation of Stock Solutions. The manganese precursor solutions were prepared by dissolving $MnSt_2$ (0.05 g) in 5 g of ODE and heated to 100 °C after being degassed under Ar flow. The zinc precursor solutions were prepared by dissolving $ZnSt_2$ (0.36 g) and HSt (designed amount) in 2.4 g of ODE. The Se precursor solutions for multiple injections were prepared by dissolving 0.0474 g of Se powder into 18 g of ODE and 0.1 g of oleyl amine at 220 °C.

Typical Synthesis of Mn:ZnSe D-Dots. Selenium powder (0.0237 g) and oleyl amine (0.05 g) in ODE (4.5 g) were loaded into a 25 mL three-neck flask and degassed at 100 °C for 20 min by bubbling with argon. The temperature was then increased to 280 °C. The falsk was kept at this temperature until selenium powder was completely dissolved. The manganese precursor solution (1 mL) was injected into the reaction flask at 280 °C. The reaction mixture was allowed to cool to 260 °C and reacted for 4 min for formation of MnSe nanoclusters. Subsequently, the reaction temperature was set at the designated temperature for ZnSe overcoating with the injection of the $ZnSt_2$ stock solution in ODE (0.5 mL). A designated amount of oleyl amine was injected into the reaction mixture to activate the zinc carboxylate. Immediately after the $ZnSt_2$ injection, the solution started to glow yellow under UV light, showing the successful overcoating of ZnSe onto the MnSe nanoclusters. If necessary, the second and third $ZnSt_2$ stock solutions (0.5 mL, respectively) could be injected, each of which would be followed by a designated amount of oleyl amine. The growth process was monitored through UV−vis and PL measurements by taking aliquots. Finally, the reaction was allowed to cool down to room temperature, and the nanocrystals were purified using methanol/hexanes extraction with the d-dots in the hexanes layer. Doped nanocrystals produced using this procedure were reproducible, and the photoluminescence quantum yield (PL QY) was in the range between 40 and 60%.

Synthesis of Large Size and Nearly Spherical Mn:ZnSe D-Dots. Selenium powder (0.0948 g) oleyl amine (0.2 g), and ODE (18 g) were loaded into a 100 mL three-neck flask and degassed at 100 °C for 20 min by bubbling with argon. The temperature was increased to 280 °C. The falsk was kept at this temperature until selenium powder was completely dissolved. Manganese precursor solution (4 mL) was injected into the reaction flask at 280 °C. The reaction mixture was allowed to cool down to 260 °C and reacted for 4 min to form MnSe nanoclusters. The reaction mixture was cooled down to 220 °C rapidly, and 2 mL of $ZnSt_2$ stock solution (3.6 g $ZnSt_2$ and 0.4 g HSt in 24 g ODE) was injected, followed by 0.4 mL of oleyl amine. The temperature was kept at 220 °C for 220 min to allow the first overcoating of ZnSe. An additional 4 mL of $ZnSt_2$ stock solution was injected, followed by 0.8 mL of oleyl amine, for the second ZnSe overcoating at 220 °C for another 220 min. The reaction mixture was cooled down to 180 °C and 20 mL of Se-ODE solution was injected, and then, heated back to 220 °C for 10 more min. Finally, 5 mL of $ZnSt_2$ stock solution was injected followed by 1 mL of oleyl amine, and the reaction mixture was maintained at 220 °C for the final 220 min. Aliquots

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(20) Chen, D. A.; Viswanatha, R.; Ong, G. L.; Xie, R. G.; Balasubramaninan, M.; Peng, X. G. *J. Am. Chem. Soc.* **2009**, *131*(26), 9333–9339.

(21) Pradhan, N.; Peng, X. G. *J. Am. Chem. Soc.* **2007**, *129*(11), 3339–3347.

(22) Yang, Y. A.; Chen, O.; Angerhofer, A.; Cao, Y. C. *J. Am. Chem. Soc.* **2008**, *130*(46), 15649–15661.

(23) Norberg, N. S.; Kittilstved, K. R.; Amonette, J. E.; Kukkadapu, R. K.; Schwartz, D. A.; Gamelin, D. R. *J. Am. Chem. Soc.* **2004**, *126*, 9387–9398.

(24) Erwin, S. C.; Zu, L. J.; Haftel, M. I.; Efros, A. L.; Kennedy, T. A.; Norris, D. J. *Nature* **2005**, *436*(7047), 91–94.

(25) Yang, Y. A.; Wu, H. M.; Williams, K. R.; Cao, Y. C. *Angew. Chem., Int. Ed.* **2005**, *44*(41), 6712–6715.

(26) Cotton, F. A.; Wilkinson, G.; Bochmann, M.; Murillo, C., *Advanced Inorganic Chemistry*, 6th ed.; Wiley−Interscience: New York, 1998; p 1248.

(27) Shen, H. B.; Wang, H. Z.; Li, X. M.; Niu, J. Z.; Wang, H.; Chen, X.; Li, L. S. *Dalton Trans.* **2009**, *47*, 10534–10540.

(28) Acharya, S.; Sarma, D. D.; Jana, N. R.; Pradhan, N. *J. Phys. Chem. Lett.* **2010**, *1*(2), 485–488.

(4 mL) were taken at different time intervals for UV−vis, photoluminescence, transmission electron microscope (TEM), and energy-dispersive X-ray spectroscopy (EDX) measurements after purification.

Purification Procedures for EDX Samples. For EDX measurements, the purification target was to remove any chemicals containing Zn, Mn, and Se that were not incorporated into the nanocrystal lattice. The resulting nanocrystals were purified using the standard methanol/hexanes extraction for at least three times, and the hexanes layer with the nanocrystals was kept and the methanol layer was discarded. Acetone mixed with $CHCl_3$ (about 3:1 volume ratio) was added into the hexanes solution to precipitate the nanocrystals. After centrifugation and decantation of the supernatant, the nanocrystal pellet on the bottom of the vial was redissolved in 2.5 mL of pyridine. The resulting nanocrystal/pyridine solution was sonicated for 1 h and placed under dark overnight. Excess hexanes were added to the nanocrystal/pyridine solution to precipitate the nanocrystals. The nanocrystal precipitate was isolated by centrifugation and decantation. The ligand exchanges with pyridine were repeated twice. The resulting powder was dried in a vacuum at 50 °C and was applied for the following EDX measurements.

Optical Measurements. UV−vis spectra were recorded on an HP 8453 UV−vis visible spectrophotometer. PL spectra were taken using a Spex Fluorolog-3 fluorometer. The PL QY was measured following the published procedure reported by Pradhan et al.[21] The excitation wavelength for measuring PL was between 350 and 400 nm, and for the PL QY determination, the excitation wavelength was chosen to be 390 nm.

Energy-Dispersive X-ray Spectroscopy (EDX). EDX was used for the elemental analysis of the inorganic nanocrystals using a Philips ESEM XL30 scanning electron microscope equipped with a field emission gun and operated at 10 kV. Each sample was measured at least three times to obtain the average value.

Transmission Electron Microscopy (TEM). TEM images were taken on a JEOL X-100 electron microscope using a 100 kV accelerating voltage at 50k magnification. Specimens were prepared by dipping a Formvar-coated copper grid into a toluene solution of the nanocrystals, and the grid with the nanocrystals was dried in air. Selected area electron diffraction pattern (SAED) was taken with a camera length of 76 cm.

Results and Discussion

Choice of Synthetic Scheme. The general synthetic scheme chosen here is "nucleation-doping", which is one of two doping strategies based on "decoupling of doping from nucleation and/or growth".[13] The dopant ions, Mn^{2+} ions, were introduced into the d-dots in the initial formation stage of the d-dots. As shown in Figure 1, the Mn dopant ions were allowed to react with Se precursor at a relatively high temperature, 260−280 °C. Prior to the addition of Mn precursor, Mn stearate ($MnSt_2$) dissolved in ocadecene (ODE), Se powder was reacted with fatty amines, such as oleyl amine using ODE as the solvent. Complete dissolution of Se powder was achieved at around 280 °C. The MnSe clusters formed in the first step (see detail below) were overcoated with ZnSe to yield Mn:ZnSe d-dots in the second step without isolation/purification of the MnSe nanoclusters formed in the first step.

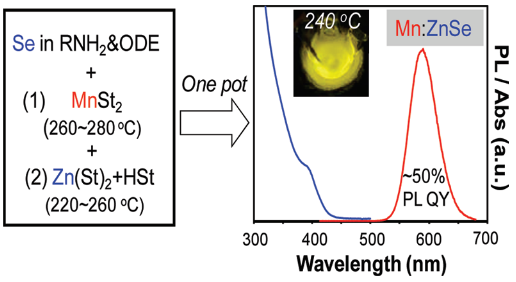

Figure 1. Schematic illustration of formation of Mn:ZnSe d-dots in one pot with air-stable starting materials. The digital picture (inset in the right panel) was taken with the radiation of a hand-held UV lamp at 240 °C. RNH_2 represents fatty amines used.

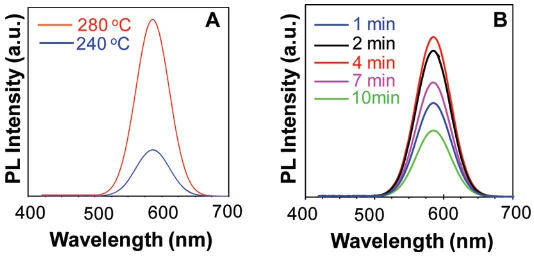

Figure 2. Influence of PL emission efficiency of Mn:ZnSe d-dots by the formation conditions of initial MnSe nanoclusters. (A) PL spectra of Mn:ZnSe d-dots grown from MnSe nanoclusters formed at 240 and 280 °C. (B) PL spectra of Mn:ZnSe d-dots vs the formation time of MnSe nanoclusters at 260 °C. Note: all temperatures mentioned in this figure are the formation temperature of MnSe nanoclusters, and the overcoating temperature of ZnSe (T_{ZnSe}) was identical for all reactions. The other reactions including the amount of zinc precursors added were kept unchanged except the reaction condition under study in each plot.

The d-dots formed by the scheme shown in Figure 1 possessed nearly 100% dopant PL at about 584 nm ($^4T_1 \rightarrow {}^6A_1$ transition for Mn^{2+} ions in ZnSe lattice).[21] The overall optical properties of the d-dots were similar to those yielded by the traditional approach using organophosphine as the Se ligands, with PL quantum yield (QY) reproducibly in the range between 40 and 60%,[21] highly emissive even at the reaction temperature (see the digital picture in Figure 1), a large Stokes's shift, and a full width at half-maximum (fwhm) of 52 nm.

Influence of PL Properties of Mn:ZnSe D-Dots by Formation Conditions of MnSe Nanoclusters. Formation of MnSe nanoclusters was found to play a critical role in determining the properties of the resulting Mn:ZnSe d-dots. When MnSe nanoclusters were formed by introducing the Mn precursor solution into the reaction flask at 280 °C (Figure 2A), the resulting d-dots possessed desired optical properties described in the above subsection. The experimental results revealed that if the temperature for the injection of the Mn precursor solution was 240 °C or below, the PL QY of the dopant emission was significantly lower than the average value, i.e., 50−60%.

Though the results mentioned in the above paragraph indicate that too low a temperature was not adequate for the formation of MnSe nanoclusters, this process could not be held at either a temperature significantly higher than 280 °C or at 280 °C for an extended period of time. Otherwise, large-sized MnSe nanocrystals would be generated (see Figure S1 in the Supporting Information), which resulted in d-dots with very poor emission properties. The optimized temperature was to inject the Mn precursor solution at 280 °C, which caused the reaction temperature to cool to 260 °C by the introduction of the relatively cold Mn precursor solution.

Even at 260 °C, growth of MnSe nanoclusters was found to be quite fast. As shown in Figure 2B, the dopant PL intensity (normalized to the same absorbance at the excitation wavelength) of the resulting d-dots increased as the formation time of MnSe nanoclusters increased at 260 °C, reached a maximum at about 4 min, and after that, it actually started to decrease. The quantitative evolution of the dopant PL intensity of the d-dots verses the reaction time for MnSe nanoclusters at 260 °C is provided in Figure S2 (see the Supporting Information), which shows a maximum region between 3 and 6 min. The size of the MnSe nanoclusters in this maximum window was too small to be detected using TEM. An indirect measurement based elemental analysis would be discussed below, which revealed the size of the MnSe nanoclusters was about 1.8 nm. If not specified, the d-dots mentioned in this report were all based on such MnSe nanoclusters formed at 260 °C for about 4 min. This size is very close to the optimal size of the MnSe nanoclusters used in the traditional approach using an organo-phosphine as the Se ligands.[21]

When organo-phosphine was used, the formation temperature of MnSe nanoclusters required 290 °C, and the formation process could hold this reaction temperature for as long as several tens of minutes.[21] This means that elimination of organo-phosphine in the current synthetic scheme activated the Se precursor, and thus somewhat softened the vigorous reaction conditions. This is consistent with the report from the Cao's group,[25] which showed that, without organo-phosphine in place, synthesis of high-quality CdSe nanocrystals could be performed at a temperature as low as 220 °C, instead of the regular 250−350 °C temperature range.

Influence of Overcoating Temperature of ZnSe Host Semiconductor (T_{ZnSe}). Recent studies indicate that doping a nanocrystal is a complex process and involves multiple elemental steps.[20] Importantly, all elemental steps were found to be highly sensitive to temperature and each possessed its own critical temperature. Relevant to designing nucleation doping, "lattice diffusion" should be the key elemental step to consider. If the dopant ions incorporated during the initial formation stage of d-dots did not diffuse during the overcoating of the host material, they were retained within the interior lattice of the final d-dots. However, if a high concentration of dopant ions were placed right next to each other within the center of a d-dot, the emission properties of the d-dots would be poor as observed previously. Early experimental results[21] further indicated that some gentle diffusion of the dopant ions into the host layer formed during overcoating would result in isolated dopant centers within the host lattice, which should thus yield high-performance d-dot emitters.

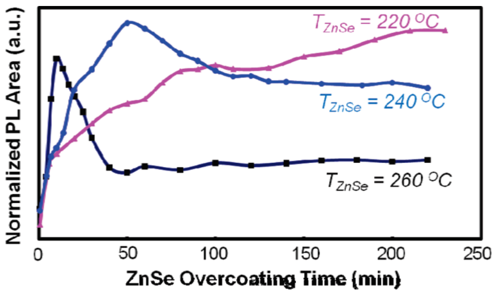

Figure 3. Temporal evolution of PL intensity of Mn:ZnSe d-dots at different ZnSe overcoating temperatures.

In light of these two competitive factors, the ZnSe overcoating temperature (T_{ZnSe}) should be chosen around the critical diffusion temperature for the system, which was reported to be ~250 °C.[20]

The results in the above subsection indicate that the MnSe nanoclusters could not be sufficiently stable with a temperature higher than 260 °C. This offered us the upper limit for determining T_{ZnSe}. If T_{ZnSe} was below 200 °C, growth of ZnSe was found to be too slow, which suggested the lower limit for T_{ZnSe}. Fortunately, the temperature range determined by these experimental conditions could satisfy the diffusion concerns mentioned in the above paragraph.

The temporal evolution of the normalized PL intensity of the d-dots formed with different T_{ZnSe} is illustrated in Figure 3. With the same type of MnSe nanoclusters cores, each PL evolution curve at a given T_{ZnSe} repeatedly showed its unique pattern. When T_{ZnSe} equals to 260 °C, the PL intensity of the d-dots possessed a sharp maximum at about 10 min. When T_{ZnSe} equals to 240 °C, a maximum could still be observed. However, the intensity of the PL maximum and the plateau PL intensity after the maximum were both higher than those at 260 °C. The reaction time needed to reach the maximum at this intermediate temperature was much longer as well, at about 50 min. At a relatively low $T_{\mathrm{ZnSe},}$ i.e., 220 °C, the PL intensity increased continuously but slowly within the experimental time frame. All of these phenomena were found to be consistent with the diffusion properties of the Mn ions in Mn:ZnSe d-dots.[20]

If the reaction at 260 °C was rapidly cooled to 220 °C after the PL reached its maximum, the normalized PL intensity of the d-dots did not decrease upon prolongated heating at 220 °C (see Figure 3S in the Supporting Information). This result means that the rapid PL intensity decrease after its maximum at 260 °C was due to the high temperature annealing, which further implies a noncontrollable diffusion at 260 °C.

One possible reason for the sharp decrease of PL QY of the dopant emission in Figure 3 for 260 and 240 °C reactions could be formation of intrinsic ZnSe nanocrystals during the overcoating of the ZnSe shell to form the d-dots. To exclude this possibility, we tried to excite the samples with a wavelength as low as 350 nm. The results implied no formation of pure ZnSe nanocrystals. It is known that, in the current solution system, pure ZnSe

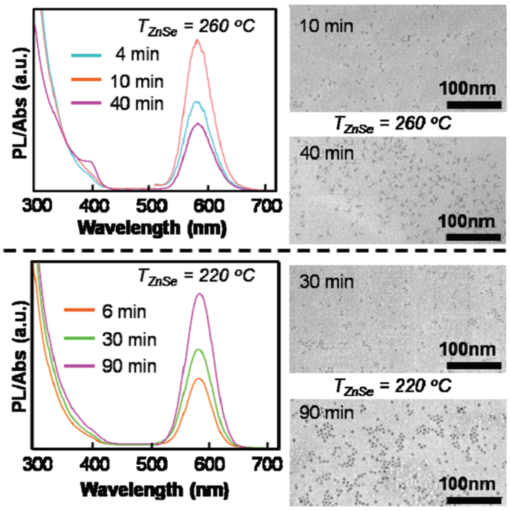

Figure 4. Temporal evolution of UV−vis, PL, and size/morphology of Mn:ZnSe d-dots at different ZnSe overcoating temperatures.

nanocrystals should be very emissive, and existence of ZnSe intrinsic dots should be readily detected by their intrinsic PL. Furthermore, control experiments were performed with the same reaction conditions except the existence of MnSe nanoclusters in the reaction solution. Within the reaction time frame, no formation of ZnSe intrinsic quantum dots were detected at all in such control reactions.

To further identify the mechanisms of the interesting temporal PL intensity evolution shown in Figure 3, the d-dots at different reaction times for different reaction temperatures were examined using UV−vis, PL and TEM. The results of two typical reaction temperatures are shown in Figure 4.

When T_{ZnSe} equals to 260 °C, the UV−vis absorption of the d-dots shifted red (Figure 4, top panel), which was consistent with the growth of ZnSe host. A similar trend was also observed at 220 °C (Figure 4, bottom panel). In comparison with the reaction with a relative low T_{ZnSe}, however, a distinguishable absorption peak at about 400 nm was observed for the reaction at 260 °C after the PL departed from the PL maximum point (10 min, see Figure 3). Because of the unique structure of the Mn:ZnSe d-dots synthesized using nucleation-doping, ZnSe of a d-dot should form quantum shell structure with a MnSe nanocluster core as the template. Consequently, the absorption spectra should not possess sharp features as those appeared in a typical quantum dot spectrum.[29,30]

The sharp feature in the spectrum taken at 40 min at 260 °C, however, might be explained by the shape change of the d-dots. As shown in Figure 4, the shape of the d-dots appeared to be branched for this specific reaction time. Experimental results observed so far[31] indicate that a branched Mn:ZnSe d-dots would often possess a relatively sharp absorption feature close to the absorption edge as the one shown in the absorption spectrum taken at 40 min for the reaction at 260 °C. Presumably, this would be a result of the pure ZnSe portion at the branches as identified previously. It should be pointed out that branched d-dots were found to show a relatively low PL QY.[31]

Table 1. Mn:Zn Atomic Ratio of D-Dots

	T_{ZnSe}					
	260 °C		240 °C		220 °C	
time (min)	10	40	50	100	90	180
Mn:Zn ratio	0.14	0.08	0.15	0.11	0.11	0.09

The decrease of PL intensity with T_{ZnSe} equals to 260 and 240 °C could also be related to loss of emissive Mn centers within the ZnSe host lattice.[20] To study this, we purified the aliquots taken at different reaction time for three T_{ZnSe} and examined them using EDX (Table 1). EDX measurements revealed that, with T_{ZnSe} equals to 220 °C, the Mn to Zn atomic ratios (Mn:Zn ratio) of the d-dots isolated at different reaction times did not change significantly. Although the reaction time difference was substantially shortened for the reactions at 240 and 260 °C, a sharp decrease of Mn:Zn atomic ratio was observed when the overcoating time past the PL maximum. These results are consistent with loss of the Mn ions of the d-dots at high $T_{\mathrm{ZnSe},}$ especially at 260 °C. For being fully conclusive, it would be great if the sizes of the d-dots corresponding to the EDX measurements could be quantitatively determined. Unfortunately, this was difficult to do because the shape of d-dots for the reactions with a high T_{ZnSe} was often branched, especially for the samples reacted for an extended period of time.

In light of the critical diffusion temperature[20] for Mn:ZnSe d-dots, 250 °C, the results in Table 1 are reasonable. Presumably, a T_{ZnSe} close to 250 °C enhanced the diffusion of the Mn ions and resulted in some loss of the Mn ions. It should be pointed out that the PL measurements of the d-dots overcoated at 260 °C (see Figure 4 (top panel) as examples) revealed pure dopant emission throughout the entire overcoating process within the experimental time frame. This means that, although "lattice diffusion" and "lattice ejection" could occur quite rapidly at a relatively high reaction temperature, complete elimination of Mn ions from the d-dots was never reached within the reaction conditions. This is quite reasonable, provided a relatively large number of Mn dopant ions were incorporated into each d-dot for this specific nucleation-doping strategy (see more results below).

Control of "Lattice Diffusion" and "Lattice Ejection" by Multiple Injections. The results in the above subsection indicate that, during the ZnSe overcoating process, there was a relatively long increasing period of PL QY as long as T_{ZnSe} was at 220−240 °C range, which indicates the shell thickness increase and partial diffusion of Mn ions into the surrounding ZnSe host shell occurred simultaneously. Presumably, the PL QY might be increased by increasing the thickness of the ZnSe overcoating layer,

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(29) Battaglia, D.; Li, J. J.; Wang, Y. J.; Peng, X. G. *Angew. Chem., Int. Ed.* **2003**, *42*(41), 5035–5039.
(30) Battaglia, D.; Blackman, B.; Peng, X. G. *J. Am. Chem. Soc.* **2005**, *127*(31), 10889–10897.
(31) Viswanatha, R.; Battaglia, D. M.; Curtis, M. E.; Mishima, T. D.; Johnson, M. B.; Peng, X. G. *Nano Res.* **2008**, *1*(2), 138–144.

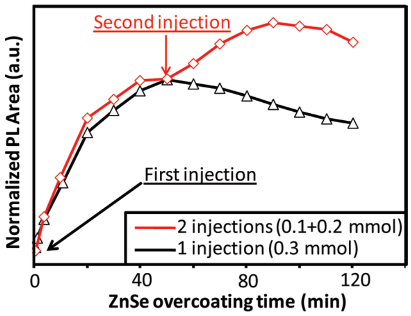

Figure 5. Temporal evolution of PL intensity of Mn:ZnSe d-dots with different injection techniques.

which should isolate the emission centers further away from the surface of the d-dots.

However, the PL QY reached with a single injection was not very high even if the amount of zinc precursor was increased. Multiple injection techniques were explored by dividing the same amount of reaction precursors into two or more injections, which increased the PL QY substantially (Figure 5). The time for the secondary injections was chosen at the position when the PL QY reached the maximum of the first injection for the given reaction temperature.

Figure 5 compared the PL QY evolution patterns for a two-injection reaction and a single-injection reaction. Though the total amounts of the precursors injected into the reaction system were same for two reactions, a significant enhancement of the PL QY was evidenced upon the second injection.

The advantage of injecting the Zn precursor solution in two portions could be explained by controlled diffusion. As discussed above, "lattice diffusion" was needed to allow some Mn ions diffusing into the surrounding ZnSe host lattice in order to obtain highly emissive d-dots.[21] However, when the Mn ions diffused into the ZnSe host lattice, they would become closer to the surface of the d-dots. As a result, they could be eliminated from the lattice through the following "lattice ejection" that occurred quite rapidly in the temperature range between 220 and 260 °C for Mn:ZnSe d-dots system.[20] In a single injection mode, growth of ZnSe overcoating layer would occur along with the diffusion of the Mn ions into the ZnSe host lattice, which promptly depleted the Zn precursors shortly after the injection. In a two-injection mode, the Zn precursor would be replenished when the growth of the nanocrystals was stopped. As a result, a continuous growth of the ZnSe host lattice would provide an additional diffusion barrier for the Mn ions. Consistent with this hypothesis, growth of ZnSe host upon the second injection was observed by UV−vis (see Figure S4 in the Supporting Information) and TEM (Figure 6).

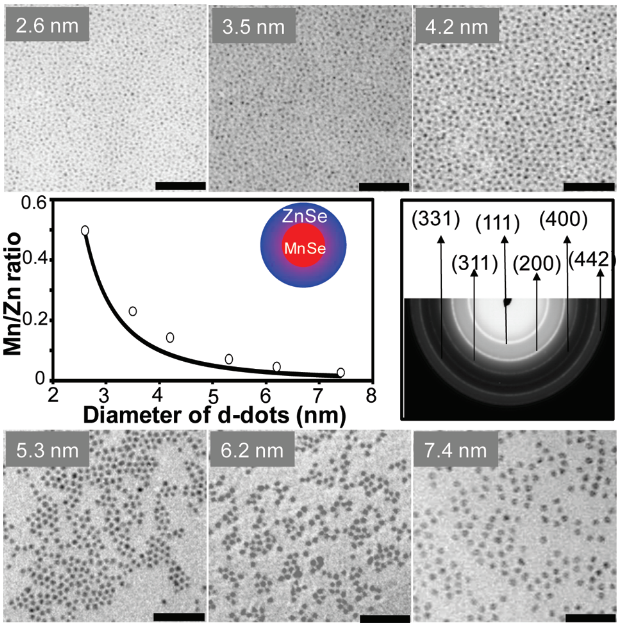

Figure 6. TEM images of Mn:ZnSe d-dots with different sizes, a typical electron diffraction pattern, and the size dependent Mn:Zn atomic ratio. The scale bars of the TEM images are 50 nm. The open circles in the Mn:Zn ratio vs the size of the d-dots plot are EDX results, and the solid line was the theoretical prediction based on a 1.8 nm MnSe nanocluster and a spherical shape of all d-dots.

Size, Shape, and Crystal Structure of D-Dots. The size of the d-dots produced by this new synthetic scheme could be well controlled. Figure 6 illustrated a series of d-dots with their sizes in the range from 2 to 8 nm, roughly the quantum confinement size range of the host semiconductor.[32,33] The size distribution of the d-dots was nearly monodisperse upon the increase in their sizes.

Usually, spherical d-dots gave better emission properties.[31] The d-dots with different sizes shown in Figure 6 were all nearly spherical in shape. However, this synthetic scheme was possible to generate branched d-dots (see Figures 4 as an example). The crystal structure of all d-dots obtained in this work was found to be zinc-blende. A typical electron diffraction pattern is given in Figure 6. The lattice constants calculated from the diffraction patterns matched well with those expected for ZnSe lattice. It was known that MnSe could exist in zinc-blende structure with its lattice constants very similar to those of ZnSe one.[13] However, the experimental results revealed that, without ZnSe overcoating, MnSe nanoclusters would eventually grow to largely sized MnSe nanocrystals—presumably through self-focusing of the MnSe nanoclusters in the solution—with their lattice structure being identified as rock salt.

Mn:Zn Atomic Ratio vs D-Dots Size. A nucleation-doping strategy[13] would imply that the Mn:Zn atomic ratio should decrease as the growth of the d-dots. If no loss of Mn ions during the ZnSe overcoating process, Mn:Zn ratio should depend on the size of the d-dots following a cubic function of the size of the d-dots (the solid line in the "Mn:Zn ratio" plot in Figure 6). The theoretical line in Figure 6 was based on a 1.8 nm MnSe nanoclusters as the initial "nuclei". The size assumption of the MnSe nanoclusters was made with the support of two experimental facts. One, the MnSe nanoclusters formed by the

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(32) Hines, M. A.; Guyot-Sionnest, P. *J. Phys. Chem. B* **1998**, *102*(19), 3655–3657.

(33) Lin, S. L.; Pradhan, N.; Wang, Y. J.; Peng, X. G. *Nano Lett.* **2004**, *4* (11), 2261–2264.

current synthetic scheme were not detectable with TEM observations, which implies that their sizes should be smaller than about 2 nm. Two, the MnSe nanoclusters identified in the traditional approach for synthesizing Mn:ZnSe d-dots using organo-phsophine as the Se ligands were about in this size range.[21]

The experimental results (open circles in the "Mn:Zn ratio" plot, Figure 6) and the theoretical prediction (solid line in the same plot) matched well within the experimental error (about 10% for EDX measurements). This indicates that Mn ions were retained within the d-dots during the ZnSe overcoating process, which is consistent with the hypothesis discussed above, i.e., partial diffusion but no noticeable loss of Mn ions during the ZnSe overcoating process.

Conclusions

In summary, highly emissive Mn:ZnSe d-dots with PL QY reproducibly between 40 and 60% were synthesized by a new approach, which eliminates the usage of pyrophoric, highly toxic, and expensive organo-phosphine and employs all air-stable and generic chemicals based on "nucleation-doping" strategy. The synthetic conditions were found to be distinguishably different from the traditional synthetic scheme reported in literature. By judiciously choosing reaction conditions, formation of MnSe nanoclusters and their overcoating by ZnSe host were both optimized to control the "lattice-diffusion" of the Mn ions incorporated into the d-dots. The key parameters for optimization included programmed reaction temperatures, reaction duration for each step, and the method for introducing reaction precursors (multiple injections verses single injection). The optimized synthetic scheme was confirmed to retain nearly all of the Mn ions within the d-dots during the ZnSe overcoating process. The results in this report not only verified feasibility on synthesizing high-quality Mn:ZnSe d-dots without pyrophoric, highly toxic, and expensive organo-phosphine, but also confirmed that rational doping chemistry could be developed on the basis of existing knowledge about nanocrystal doping.

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Supporting Information Available: Supporting results mentioned in the text (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.