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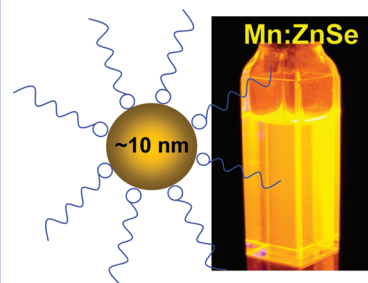
# An Alternate Route to High-Quality ZnSe and Mn-Doped ZnSe Nanocrystals

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**ABSTRACT** We report here a synthetic route for high-quality Mn-doped ZnSe nanocrystals using selenourea as a selenium source, avoiding the more conventional route using tributylphosphine (TBP) that restricts the growth of spherical ZnSe nanocrystals below 5 nm in size, besides being highly toxic and pyrophoric. Spherical ZnSe nanocrystals with unprecedented sizes (up to 12 nm) are synthesized, the large size of the host helps to keep dopant ions well inside the nanocrystal, leading to intense and stable dopant emission. Mn-doped ZnSe nanocrystals with more than 50% quantum yield (QY) are synthesized in this method and found to be stable both in aqueous and nonaqueous dispersions for months.

**SECTION** Nanoparticles and Nanostructures



ZnSe is a wide band gap semiconductor material with bulk band gap of 2.7 eV.<sup>1</sup> It emits in the violet-blue window when the size is reduced to below the Bohr excitonic radius.<sup>2</sup> In recent developments, ZnSe has been targeted as an efficient semiconductor host to dope different transition metal ions extending its emission window from violet blue to the red end of the visible spectrum.<sup>3–7</sup> For the case of Mn doping, the strong electronic interaction between Mn<sup>2+</sup> d states and s-p states of the host generates intermediate energy states in the system through which the host generated exciton relaxes (<sup>4</sup>T<sub>1</sub> → <sup>6</sup>A<sub>1</sub>) resulting in a new emission centered at 585 nm.<sup>3,7–11</sup> Being excited in the blue window corresponding to the band gap of the host, this new dopant-induced emission remains widely separated from the absorption edge. This avoids the reabsorption or the self-absorption process and makes the system ideal for different optical applications.<sup>12</sup> Additionally, this also generates a cadmium-free nanocrystal emitter, which can be used as nontoxic labels for different biological<sup>13</sup> and other applications.

Synthesis of different size and shape of ZnSe nanocrystals are already reported in the literature.<sup>2,6,14–18</sup> Early attempts by Hines et al.<sup>2</sup> in 1998 using organometallic zinc precursors and later the well-developed method using trioctylphosphine oxide (TOPO) reported size tunable blue emitting ZnSe nanocrystals. In early 2000, Mn<sup>2+</sup> ions were doped to ZnSe nanocrystals using organometallic Mn as dopant precursors, resulting in highly intense dopant emission (quantum yield, QY, 22 %).<sup>4</sup> Later, Li et al. developed a mild synthetic route replacing the organometallic zinc with common zinc carboxylate salts and TOPO with the less expensive solvent 1-octadecene (ODE).<sup>14</sup> Mn<sup>2+</sup> ions are also doped to these ZnSe

nanocrystals using Mn carboxylate as the Mn precursor and reported more than 50 % QY of the dopant emission.<sup>5</sup>

For all the above-reported synthetic methods, the key source of selenium is the elemental selenium dissolved in tributylphosphine (TBP). TBP is a toxic and pyrophoric chemical, and its transportation and supply are restricted in many places. Moreover, using TBPSe as the selenium source, it has so far not been possible to grow spherical ZnSe nanocrystals beyond 5 nm diameter. It has been found that any attempt to grow nanocrystals beyond this size leads to anisotropic growth of faceted and/or rod-shaped particles.<sup>14</sup> However, larger sized host nanocrystals are preferred for efficient doping processes so that defects generated by dopants can relax better within the crystal and also the dopant ions can stay much deeper inside the host lattice to generate efficient emissions. There are several other likely advantages of such large, highly luminescent nanoparticles being explored in recent times, including the possibility of avoiding the phenomenon of blinking of the emission. Hence, making the synthetic method TBP free and growing larger ZnSe hosts for doping are central to developing useful, optically active nanomaterials. However, these important objectives have not been realized so far. We explore here selenourea as an alternate selenium source, which not only helps the growth of ZnSe nanocrystals beyond 10 nm, but also facilitates incorporation of Mn<sup>2+</sup> ions deep inside the nanocrystals, leading to an efficient and stable dopant emission. Unlike TBPSe, introduction of selenourea solution in oleyl amine

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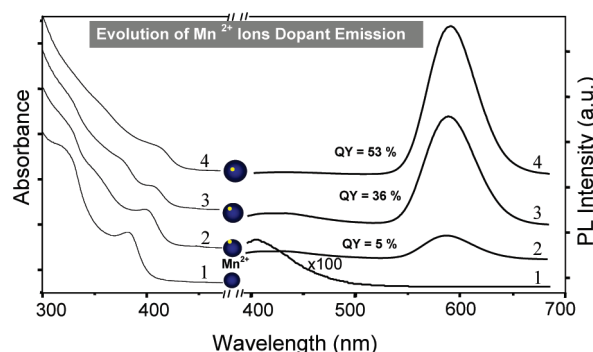
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allows tuning the size of ZnSe nanocrystals from 3 to 12 nm without any anisotropic growth. The dopant emission is stable in air and shows more than 50 % QY both in organic as well as aqueous dispersions.

Selenourea is a known source to release selenium ions,<sup>15,19–25</sup> and this release can be finely controlled by controlling the reaction condition and the injection temperature. We took the advantage of this control to synthesize ZnSe nanocrystals with a high-temperature injection technique. It is known that selenourea in long-chain fatty amines helps the formation of one-dimensional (1D) nanowires.<sup>15,19</sup> We circumvented this problem by restricting the amount of free amines by diluting it with an excess amount of a noncoordinating solvent, namely, ODE. This hinders the 1D growth and facilitates the formation of spherical ZnSe nanocrystals. We carried out a series of reactions, systematically changing different components, in order to identify the key ingredients in this synthetic procedure that allow us to go beyond the existing size limit (~5–6 nm) for spherical ZnSe nanocrystals. Our results establish that the precursor selenourea itself and its presence in excess amount in the reaction mixture are most crucial for larger size growth of ZnSe nanocrystals. It is to be noted here that selenourea is not only a source of selenide ions for the crystal growth, but it also contains an amine group that can coordinate zinc sites of a growing nanocrystal, acting as temporary ligand and thereby effectively increasing the amine concentration in the reaction mixture. We have found that an increase in the amount of free amines (oleyl or hexadecyl) facilitates the anisotropic growth, as in the presence of TBPSe. It appears that TBPSe, which binds strongly to the ZnSe nanocrystals, as well as an enhanced amount of amine in the reaction mixture restrict isotropic crystal growth via preferential binding on certain facets of growing nanocrystals. In our synthetic process, oleylamine has been chosen as the solvent for selenourea because of its existence in the liquid phase at room temperature, leading to an ease of handling. Other amines (hexadecyl or octadecyl) also give similar results.

The synthesis of ZnSe nanocrystals is carried out by the injection of selenium precursors (selenourea in oleylamine) to zinc precursors (Zn-stearate, in ODE) at the desired temperature (~260 °C). Amines are initially not taken along with Zn-stearate in the mixture to avoid ZnO formation. Aliquots of the samples from the reaction mixture are periodically taken for spectral measurements. ZnSe nanocrystals nucleate at this temperature within a minute or two, as evidenced by absorption as well as emission spectra of the aliquots. For further growth processes, the temperature is reduced to 240 °C, and additional amounts of zinc precursors are phase-wise injected. For doping of Mn<sup>2+</sup> ions, the required amount of Mn precursors (Mn-stearate in ODE) is injected in to the reaction mixture after the host nucleations and annealed for 5–10 min until the appearance of the Mn dopant emission at 580 nm. To grow the Mn-doped nanocrystals further, zinc precursors are injected in several steps for the overgrowth of dopant-adsorbed host nanocrystals.

Figure 1 shows typical absorption and photoluminescence (PL) spectra reflecting the evolution of ZnSe hosts and Mn-doped ZnSe nanocrystals at various stages of growth in

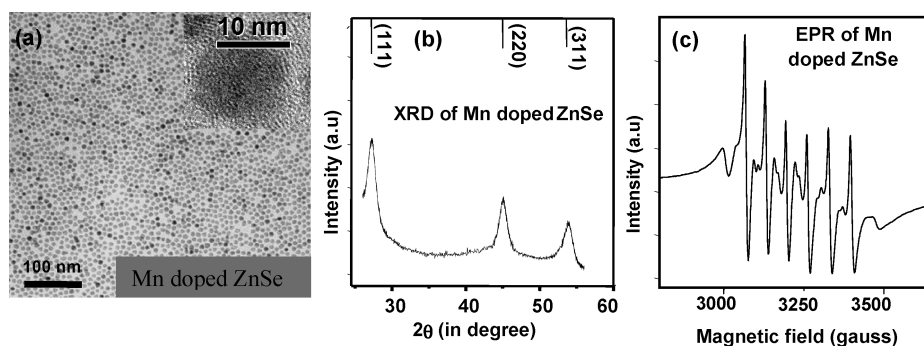


**Figure 1.** UV–visible and PL spectra of Mn-doped ZnSe nanocrystals. Initially ZnSe nanocrystals are synthesized by injection of excess selenium source at 260 °C and further growth by manual injection of zinc precursors at 240 °C. The bottom spectra (1) corresponds to undoped ZnSe, the next one (2) is that after Mn introduction, and the top two spectra (3 and 4) are during overgrowth of ZnSe nanocrystals. Excitation wavelength is 370 nm.

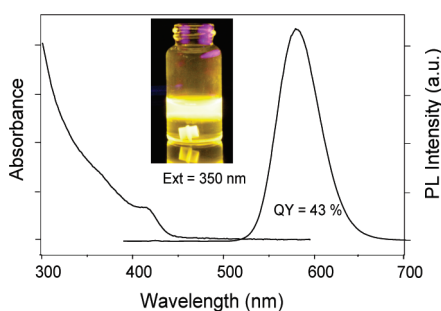
the selenium injection synthetic process. As shown in spectra 2–4 of Figure 1, the QY of the dopant emission increases from 5 % to a saturation value of about 53 % during this overgrowth.

Figure 2a shows a transmission electron microscopy (TEM) micrograph of ~10 nm diameter Mn-doped ZnSe nanocrystals, corresponding to the final spectrum of Figure 1 with 53 % QY (labeled a). X-ray diffraction (XRD) of this sample (Figure 2b) shows the sample to be in the cubic zinc blende structure. The calculated *d* spacings for different planes (see caption of Figure 2) agree well with those of the bulk ZnSe. We estimate the size of these nanocrystals to be 8.2 nm (average) from the broadening of the diffraction peaks, which is nearly close to the value obtained from TEM (Figure 2a, inset). In order to understand the location of Mn<sup>2+</sup> ions in the ZnSe host matrix, we have recorded the electron paramagnetic resonance (EPR) spectrum of these nanocrystals (Figure 2c). The six-line spectrum resulting from the hyperfine interaction of the unpaired electrons with <sup>55</sup>Mn nuclear spin (*I* = 5/2) provides evidence for well-dispersed doping without any clustering of Mn<sup>2+</sup>. The hyperfine splitting of 65 G and *g* = 2.003 determined from the EPR spectrum is in close agreement with the literature data for Mn<sup>2+</sup> ions in (tetrahedral sites of the) cubic zinc blende lattice.<sup>6,11</sup> When Mn<sup>2+</sup> ions are located on the particle surface, an increase of the hyperfine splitting to approximately 95 G is expected,<sup>26</sup> which is not observed here. However, the asymmetric broad feature in the overall spectrum is possibly due to the presence of a trace amount of Mn-stearate along with doped nanocrystals. A control EPR spectrum of Mn-stearate has been provided in the Supporting Information (Figure S1). These results clearly establish the formation of high-quality, large, and Mn-doped ZnSe nanocrystals with dopants in substitutional tetrahedral sites, deep inside the core region.

These doped nanocrystals can be made water-soluble using mercaptocarboxylic acid (MPA), poly(acrylic acid), or polyacrylamine as exchange ligands.<sup>15</sup> MPA-capped Mn-doped ZnSe retains its original emission efficiency in water and is stable under air and UV-irradiation. Figure 3 shows the UV–visible absorption and PL spectra of MPA-capped



**Figure 2.** (a) TEM picture of  $\sim 10$  nm ZnSe nanocrystals. Inset is an enlarged picture of a single nanocrystal. (b) XRD of Mn-doped ZnSe nanocrystals showing the cubic Zinc blende structure, and calculated  $d$ -spacings are 3.28, 2.0, and 1.71 Å for (111), (220) and (311) planes, respectively. (c) EPR spectra of Mn-doped ZnSe measured at 123 K.



**Figure 3.** UV–visible and PL spectra of water-soluble MPA-capped Mn-doped ZnSe nanocrystals. Inset is a digital picture of Mn-doped ZnSe nanocrystals transferred from chloroform to the aqueous layer.

water-soluble Mn-doped ZnSe nanocrystals of  $\sim 10$  nm diameter, which are stable for more than a month.

In conclusion, we report here the synthesis of large ( $> 10$  nm) spherical ZnSe particles, which has not been possible so far using existing methods in the literature. These large ZnSe nanocrystals are shown to be a very efficient host for dopant  $\text{Mn}^{2+}$  ions, leading to intense dopant emission with more than 50 % QY. This synthetic method avoids the use of the toxic and pyrophoric TBP source and hence is more suitable for scaling up and more widespread applications. Even though other selenium precursors have been used for synthesis of metal selenides,<sup>27,28</sup> we found here that selenourea is an ideal Se precursor for controlled release of Se and to make nanocrystals larger. The Mn-doped nanocrystals are comparable to the best reported nanocrystals of its kind in terms of PL efficiency, long-term stability, surface functionalization, and stability in aqueous dispersion.

## EXPERIMENTAL METHODS

**Synthesis of ZnSe nanoparticles:** 0.063 g (0.1 mmol) zinc stearate ( $\text{ZnSt}_2$ ) in 5 mL of ODE solvent was loaded in a three-necked flask. The mixture was purged with nitrogen for 15 min to make it free from air and create an inert atmosphere. Then the solution was heated to 250 °C, 0.2 mmol of selenourea (dissolved in oleylamine) was injected rapidly into it, and the temperature was quickly reduced to 220 °C. The formed ZnSe nanocrystals were allowed to grow at that

temperature followed by subsequent UV and PL measurements. Subsequent growths were done by alternate injection of both selenium and zinc precursors to get the desired size of nanocrystals. The complete reaction took 30–40 min to grow the nanocrystals up to 10–12 nm.

**Synthesis of Mn doped ZnSe:** In a typical synthesis, 0.063 g (0.1 mmol)  $\text{ZnSt}_2$  and 5 mL ODE solvent were loaded in a three-necked flask, degassed, and heated to 260 °C. At this temperature, 0.3 mmol of selenourea in 0.6 mL oleylamine was rapidly injected into the reaction flask. The temperature was then cooled to 240 °C, and 0.002 g (0.03 mmol) of Mn-stearate dissolved in 0.5 mL of ODE was injected. Once the doping emission peak appeared, the temperature was increased to 260 °C, and nanocrystals were further grown by adding additional zinc precursors. A stock solution of  $\text{ZnSt}_2$  and stearic acid (SA) in ODE was prepared with 0.63 g of  $\text{ZnSt}_2$  (1 mmol) and 0.28 g SA (1 mmol) dissolved in 10 mL of ODE. Five milliliters of this stock solution was injected phase-wise in two steps at a 15 min interval. The injection was carried out at 260 °C, and growth occurred at 240 °C. Finally, the nanocrystals were harvested using acetone as the non-solvent. The QY was measured using a standard organic dye, quinine sulfate, in methanol solution. The QY of the nanocrystals after repeated purifications was usually found to be between 40 % and 50 % with the best value obtained reaching up to 53 %.

**SUPPORTING INFORMATION AVAILABLE** EPR of Mn stearate powder, HRTEM and SAED pattern of Mn-doped ZnSe nanocrystals, details of materials used, experimental techniques, and specifications of instruments used. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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