

Electronic Supplementary Information

Thermal Stability of Mn²⁺ Ion Luminescence in Mn-Doped Core/Shell Quantum Dots

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Synthesis of Mn-doped quantum dots (QDs)

Chemicals: Zinc stearate (ZnSt₂, ZnO 12.5-14%), stearic acid (HSt, 95%), tetramethylammonium hydroxide (TMAH, 25% w/w in methanol), and octadecylamine (ODA, 95%) were commercially available from Alpha Aesar. Selenium powder (Se, 200 mesh, 99.999%), oleyl amine (OLA, 70%), and 1-Octadecene (ODE, 90%) were purchased from Aldrich. Sulfur powders (S, 99.99%), Sodium borohydride (NaBH₄, AR), and manganese chloride (MnCl₂·4H₂O, AR) were purchased from Aladdin company. All the chemicals were used directly without further purification.

Preparation of manganese stearate (MnSt₂): The manganese precursor of MnSt₂ was prepared in a similar method to that reported in previous work.¹ In a typical process, 2.85 g of HSt was dissolved in 25 mL of methanol, loaded into a 100 mL three necked flask, heated up to 50–60 °C to obtain a clear solution in air, and followed by cooling to ~40 °C. Then a TMAH solution (obtained by dissolving 3.64 g of TMAH (25% w/w) in 3 mL of methanol) was mixed with the HSt solution. The obtained mixture was stirred for 20 min to make the reaction complete. Then 0.99 g of MnCl₂·4H₂O dissolved in 5 mL of methanol was introduced into the mixture dropwise with vigorous stirring to obtain a white precipitate of MnSt₂. The resultant precipitate was washed repeatedly with hot methanol and dried under vacuum.

Preparation of stock solutions for Mn:ZnS QDs: S stock solution was prepared by adding 0.039 g of S to 4 mL of ODE with heating to clear (ODE-S solution), then 0.4 g of ODA was mixed with the ODE-S solution and heated until the solution turned to colorless. Zinc precursor solutions were prepared by using 0.70 g of ZnSt₂ dissolved in 7 mL of ODE with heating to colorless.

Preparation of stock solutions for Mn:ZnSe and Mn:ZnSeS QDs: The Se precursor solution was prepared by dissolving 0.075 g of Se and 0.038 g of NaBH₄ in 3 mL of OLA. The Zn precursor solution was prepared by adding 0.45 g of ZnSt₂ and 0.05 g of HSt in 3 mL of ODE. The S precursor solution (0.1 mol/L) was prepared by adding 0.032 g of S and 10 mL of ODE to a 20 mL glass vial followed by heating with a hot gun until the solution turned clear. It was stored at room temperature.

Synthesis of Mn:ZnS QDs: For a typical synthesis of MnS/ZnS core/shell QDs, 10 mL of ODE and 0.03 g of MnSt₂ was loaded into a 50 mL three-necked flask and degassed at 110 °C for 15 min by bubbling with argon. The temperature was then raised to 270 °C and the S stock solution was swiftly injected into the reaction flask. Immediately after the injection, the color of the solution turned faint yellow, showing the formation of MnS nanoclusters. The reaction temperature was swiftly cooled to 170 °C, in order to obtain small, monodispersed MnS core. 2 mL of Zinc precursor solutions was added into the reaction flask and then increased to 260 °C for ZnS overcoating, and maintained at that temperature for 15 min, the obtained QDs referred to as sample Mn:ZnS-1. Then the remaining Zinc precursor solutions (5 mL) was added dropwise to the reaction flask at 260 °C in 2 mL and 3 mL portions at intervals of 15 min to obtain QDs with different ZnS shell thicknesses (referred to as samples Mn:ZnS-2 and Mn:ZnS-3, respectively), followed by cooling to room temperature. The QDs were precipitated using acetone.

Synthesis of Mn:ZnSe QDs: 5 mL of ODE, 0.020 g of MnSt₂, and 0.034 g of HSt were loaded into a 25 mL three-neck flask and degassed at 110 °C for 20 min by bubbling with argon. The temperature was then raised to 275 °C. In a separate vial, all Se precursor solution was injected into the above reaction flask. The reaction mixture was allowed to cool to 260 °C quickly and reacted for 3 min to form the MnSe nanoclusters. Subsequently, 0.5 mL of heated Zn precursor solution was injected into the reaction flask. Then, 0.5 mL of the second and third Zn precursor solutions were injected after 10 min intervals, respectively. Finally, the reaction was cooled to room temperature, and the QDs were purified at least three times until the methanol layer was clear, and then the hexanes layer with the QDs was kept and the methanol layer was discarded.

Synthesis of Mn:ZnSeS QDs: 5 mL of ODE, 0.020 g of MnSt₂, and 0.034 g of HSt were loaded into a 25 mL three-neck flask and degassed at 110 °C for 20 min by bubbling with argon. The

temperature was then raised to 275 °C. In a separate vial, all Se precursor solution was injected into the above reaction flask. The reaction mixture was allowed to cool to 260 °C quickly and reacted for 1.5 min to form the MnSe nanoclusters. Then, 0.5 mL of heated Zn precursor solution was injected into the reaction flask, followed by 0.4 mL of S precursor. The reaction was kept at 260 °C for 10 min. Then, the second and third Zn (0.5 mL) and S (0.4 mL) precursor solutions were injected after 10 min intervals, respectively, sample Mn:ZnSe_{0.73}S_{0.27} QDs were obtained. When the S precursor solutions were changed to 0.6 mL, sample Mn:ZnSe_{0.22}S_{0.78} QDs were obtained. Finally, the reaction was cooled to room temperature, and the QDs were purified at least three times until the methanol layer was clear, and then the hexanes layer with the QDs was kept and the methanol layer was discarded.

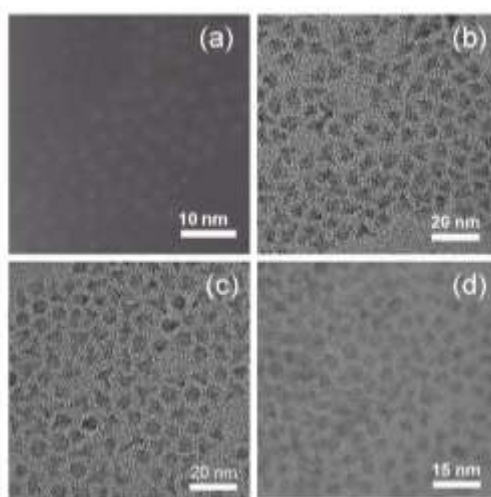


Fig. S1 TEM images of MnS core (a), MnSe/ZnSe (b), MnSe/ZnSe_{0.73}S_{0.27} (c), and MnSe/ZnSe_{0.22}S_{0.78} (d) core/shell QDs. The average diameters were estimated to be 2.3, 5.9, 5.8, and 5.1 nm, respectively. MnSe cores were not detectable with TEM observations. The diameters of the MnSe cores were determined to be 1.8 nm, on the basis of our previous works.^{1,2} The thicknesses of the shells were estimated to be about 6.2, 6.3, and 5.2 MLs, based on the TEM images and one monolayer thickness of 0.33 and 0.32 nm for ZnSe and ZnSeS materials.

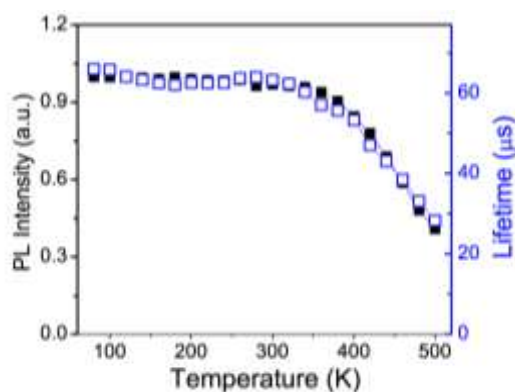


Fig. S2 Temperature dependence of the integrated PL intensities (black solid squares) and decay times (blue open squares) of Mn^{2+} ions in Mn:ZnSe QDs.

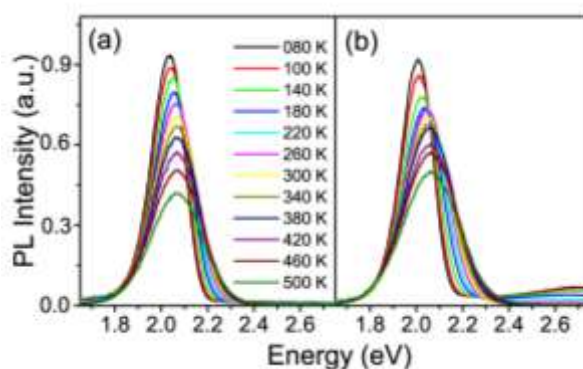


Fig. S3 PL spectra of Mn:ZnSe_{0.73}S_{0.27} QDs (a) and Mn:ZnSe_{0.22}S_{0.78} QDs (b) at different temperatures from 80 to 500 K, under excitation at 280 nm. The broad emission with peak center at about 2.7 eV in Mn:ZnSe_{0.22}S_{0.78} QDs was due to the defect emission, which emanated from the host^{3,4} and was completely quenched, when the temperature was over 220 K.

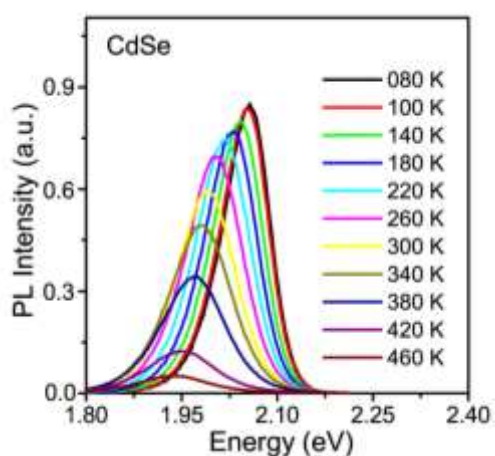


Fig. S4 PL spectra of CdSe/CdS/ZnS core/shell QDs at different temperatures from 80 to 460 K, under excitation at 280 nm.

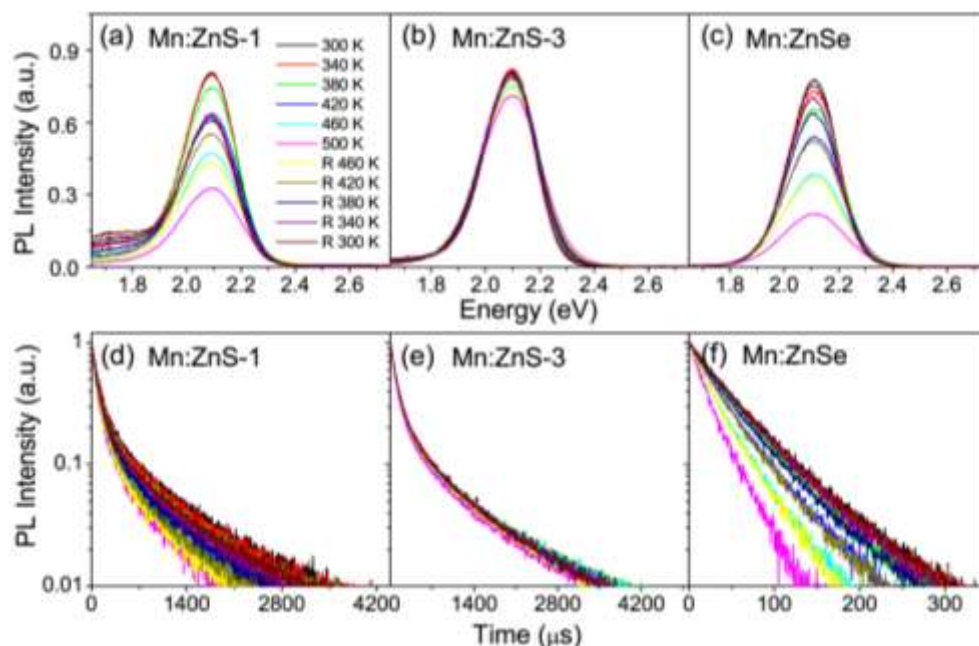


Fig. S5 Temperature-dependent PL spectra (top) and decay curves (bottom) of Mn:ZnS-1 (3.4 ML ZnS) (a,d), Mn:ZnS-3 (6.4 ML ZnS) (b,e), and Mn:ZnSe (c,f) core/shell QDs, heating from 300 to 500 K and then cooling from 500 to 300 K, under excitation at 280 nm.

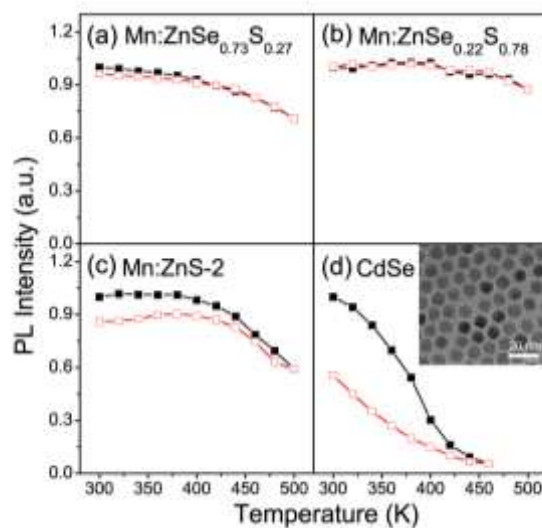


Fig. S6 Temperature-dependent integrated PL intensities of Mn:ZnSe_{0.73}S_{0.27} (a), Mn:ZnSe_{0.22}S_{0.78} (b), Mn:ZnS-2 (4.5 ML ZnS) (c), and CdSe/CdS/ZnS (d) core/shell QDs. Black solid squares refer to the heating processes, while red open squares represent cooling processes. TEM images of the CdSe/CdS/ZnS core/shell QDs are shown in the inset.

References:

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