Electronic Supplementary Information

Temperature-dependent Photoluminescence Properties of Mn:ZnCdS Quantum Dots

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The representative synthesis procedure for the Mn:ZnCdS QDs: 0.03 g of $MnSt_2$ and 12 mL of ODE were transferred into a 100 mL three necked flask and degassed for 20 min by bubbling Ar at 100 ^oC followed by heating up to 260 ^oC. Then the S stock solution (0.045 g of S powder and 0.2 mL of DDT in 3 mL of ODE) was injected rapidly into the flask to form MnS nanoclusters and the color of the solution turned faint yellow. Subsequently, $ZnSt_2$ solution (0.06 g of $ZnSt_2$ and 2 mL of ODE) was added to the reaction at 260 ^oC followed by heating up to 280 ^oC and maintaining the temperature for 10 min to coat the nanoclusters with ZnS, which allowed the growth of the ZnS buffer layer around the MnS core and favored the diffusion of the Mn^{2+} ions. Then small aliquots were removed from the reaction solution with a syringe to character the size of the MnS/ZnS QDs before the CdS shell overcoat. Then the stock solution of cadmium precursor (0.5 g of $CdSt_2$ and 6 mL of ODE) was injected by adding 2 mL after 15 min intervals three times added at 230 ^oC to obtain QDs with thick CdS shell thicknesses (show the PL QY of ～70% at room temperature, the PL quantum yield (QY) measurements are shown in this supporting information), followed by cooling to room temperature. In order to understand the thermal quenching mechanism, another sample of Mn:ZnCdS QDs with a thin CdS shell were needed. The sample was obtained by removing 1 mL liquid from the reaction solution with a syringe before the second overcoating of CdS shell during above synthesis process for the first sample. It shows the PL QY of ～13% at room temperature due to the thin shell thickness.

Then we come to the point why we synthesized the Mn:ZnCdS QDs with the core-shell structure of MnS/ZnS/CdS. The traditional synthetic approaches for the doped QDs (d-dots) have been generally synthesized based on a reaction system with both dopant ions and competitive host ions, which is difficult to control. As a result, the obtained d-dots are often mixed with a significant portion of undoped NCs, which was substantially improved by peng's group who have reported the synthesis of Mn:ZnSe d-dots using a nucleation-doping strategy with the structure of MnSe/ZnSe (*J. Am. Chem. Soc.,* 2007, **129**, 3339). During the overcoating of ZnSe shells on MnSe cores, some of Mn^{2+} ions would diffuse from the MnSe core to the ZnSe shell due to the high activity of the small MnSe cores and the high overcoating temperature, which leads to the formation of Mn:ZnSe interface layers. It was confirmed that both the energy transfer from the excitons in ZnSe host to Mn^{2+} ions and the Mn^{2+} ions emission processes occurred at the interface of Mn:ZnSe layers, with the dopant ions as the emission centers and the pure host overcoating layer as the absorption zone. They have obtained an extremely high PL QY of Mn:ZnSe d-dots using the nucleation-doping strategy. Thus, we attempt to synthesize the

Mn:CdS QD using the nucleation-doping strategy with the structure of MnS/CdS. However, the obtained QDs show poor optical properties due to the large lattice mismatch between MnS and CdS. Therefore, a ZnS buffer layer was introduced to reduce the local strains.

It should be point out that, for our Mn:ZnCdS QDs synthesized by nucleation-doping strategy with the designed structure of MnS/ZnS/CdS, the doping concentration of Mn ions can not be accurately determined because it is difficulty to distinguish the Mn^{2+} ions whether still stayed in MnS cores or have diffused to ZnS buffer layer and CdS shell during the synthesis process. However, we consider that the concentration in the two samples with various CdS shell thickness should be very close since they have the same MnS core and ZnS buffer layer and the diffusion process of the Mn ions, which only occurred during the first overcoating of the thin shell of about 2-3 ML.

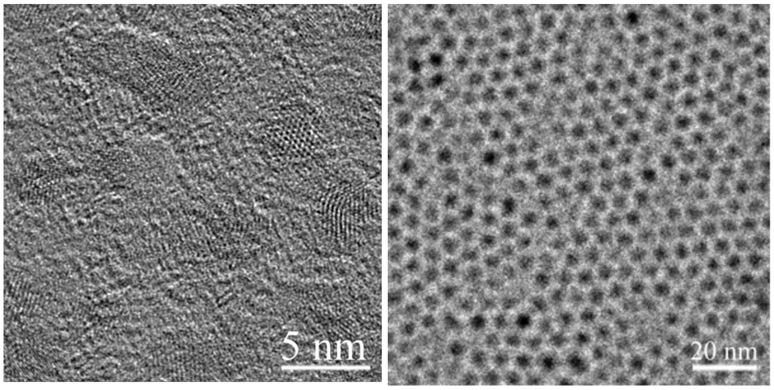

Figure S1. The typical TEM images recorded from MnS/ZnS QDs without CdS shell (left) and the Mn:ZnCdS QDs with thin shell thickness (right), the sizes are estimated to be about 2.8 nm and 3.4 nm, respectively.

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Calculation of the ZnS buffer layer thicknesses

To calculate the ZnS buffer layer thicknesses, we assume that all of the precursors are participated in the growth of nanocrystals (NCs). Thus, the total amount (N) of NCs is determined by used $MnSt_2$ (0.05 mmol). Based on the precursor ratio ($ZnSt_2$:$MnSt_2$) of 2:1 and the size of 2.8 nm detected by TEM for the sample of MnS/ZnS which without CdS shell, the radii of the MnS core can be estimated as:

$$r_{MnS}^3 = r_{MnS/ZnS}^3 - \frac{V_{ZnS}}{\frac{4}{3}\pi N} = r_{MnS/ZnS}^3 - \frac{3m_{ZnS}}{4\pi D_{ZnS} N}$$

$$N = \frac{n_{MnS} \times M_{MnS}}{\frac{4}{3}\pi r_{MnS}^3 \times D_{MnS}}$$

Here, N is the number of the MnS nuclei in the reaction system, n_{MnS} is the mole amount of Mn^{2+} used in the reaction (0.05 mmol), $r_{MnS/ZnS}$ is the radii of MnS/ZnS NCs (1.4 nm, as shown in the Figure S1), which is coated by a thin ZnS layer with 0.06 g $ZnSt_2$ precursor. D_{ZnS} and D_{MnS} are the bulk densities of ZnS and MnS (*i.e.* 4.1 and 4.0 g/cm^2), respectively. M_{ZnS} and M_{MnS} are the molar mass of ZnS and MnS (*i.e* 97.5 and 144.5 g/mol), respectively. Then the r_{MnS} is calculated to be 1.05 nm. Considering a thickness of 0.67 nm for 1 ML of the ZnS layer in our case, the thickness of the ZnS buffer layer is estimated to be ~1.1 MLs ((2.8-2.1)/0.62=1.1).

The PL quantum yield (QY) measurements:

The PL QY was recorded using a Horiba Jobin Yvon Fluromax-4P with Quantum-Yield accessory. In this system, the QY is, by definition, photons emitted to photons absorbed:

$$QY = \frac{E_a - E_c}{L_c - L_a}$$

Where E_{a} is the integrated luminescence of the sample caused by direct excitation, and E_{c} is the integrated luminescence from a pure solvent (only a blank) in the integrating sphere. The term L_{c} is the integrated Rayleigh excitation profile from pure solvent in integrating sphere. L_{a} is the Rayleigh excitation profile from the sample.

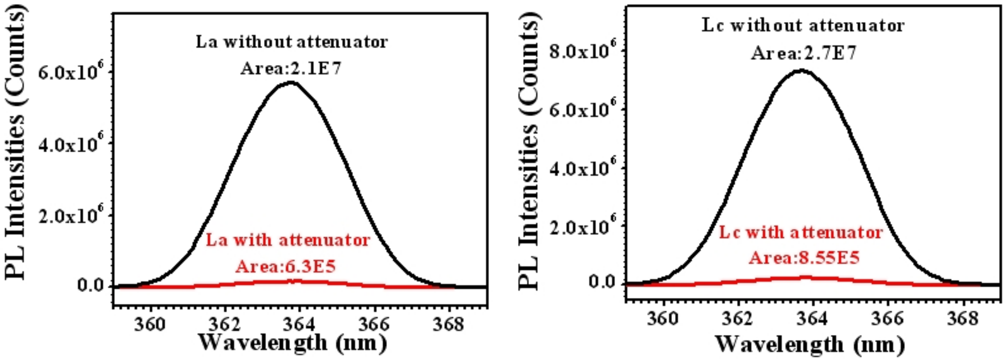
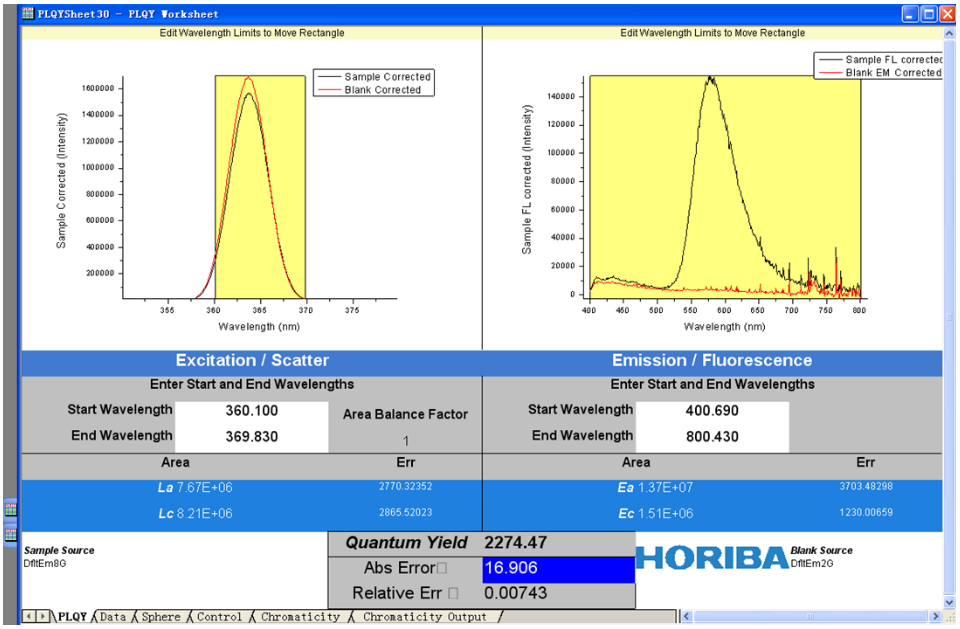


Figure S2. The integrated Rayleigh excitation profiles from pure solvent (up), and sample (down) in integrating sphere without (black line) and with (red line) attenuator. The ratio of the two areas is ～32.3.

In order to adjust the Rayleigh excitation peak for the pure solvent to the desired count rate (suggested value≈10^6 counts/s), the attenuator with a factor of ～32.3 at the wavelength of 365 nm (as shown in Figure S2) was used when collecting the L_{c} and L_{a}, and then taken out for collecting the E_{a} and E_{c}. At these conditions, the results appear in below spreadsheets (as shown in Figure S3, which was recorded from our typical experiments for the QY measurement of the sample with a thick CdS shell).



Excitation / Scatter

Enter Start and End Wavelengths

Start Wavelength 360.100

End Wavelength 369.830

Area Balance Factor 1

Area	Err
La 7.67E+06	2770.32352
Lc 8.21E+06	2865.52023

Emission / Fluorescence

Enter Start and End Wavelengths

Start Wavelength 400.690

End Wavelength 800.430

Area	Err
Ea 1.37E+07	3703.48298
Ec 1.51E+06	1230.00659

Sample Source DfltEm8G

Quantum Yield 2274.47

Abs Error 16.906

Relative Err 0.00743

Blank Source DfltEm2G

Figure S3.

So, the real QY of the sample ($QY_{(r)}$) can be given as:

$$QY_{(r)} = \frac{E_{a(r)} - E_{c(r)}}{L_{c(r)} - L_{a(r)}} = \frac{E_{a(m)} - E_{c(m)}}{(L_{c(m)} - L_{a(m)}) \times 32.3} = QY_{(m)} / 32.3 = 2274 / 32.3 = 70$$

Where $E_{a(r)}$, $E_{c(r)}$, $L_{c(r)}$, and $L_{a(r)}$ are the real values of the E_a, E_c, L_c, and L_a collected without the attenuator, and $E_{a(m)}$, $E_{c(m)}$, $L_{c(m)}$, $L_{a(m)}$, and $QY_{(m)}$ are the measured values of the E_a, E_c, L_c, L_a, and QY, respectively. The PL QY of d-dots was repeat tested for more than ten times with various concentrations, and the obtained values are within 8% errors.