

**Electronic Supplementary Information**

**Highly Efficient and Well-Resolved Mn<sup>2+</sup> Ions Emission in MnS/ZnS/CdS  
Quantum Dots**

Sheng Cao<sup>a,b,ζ</sup>, Jinju Zheng<sup>b,c,ζ</sup>, Jialong Zhao<sup>d</sup>, Lin Wang<sup>b</sup>, Fengmei Gao<sup>b</sup>, Guodong Wei<sup>b</sup>, Ruosheng Zeng<sup>e</sup>,

Linhai Tian<sup>\*a</sup> and Weiyu Yang<sup>\*b</sup>

*ζ* Equal Contribution authors

<sup>a</sup> *Research Institute of Surface Engineering, Taiyuan University of Technology, Taiyuan, 030024, People's Republic of China.*

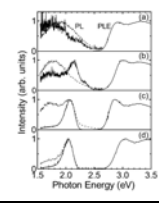
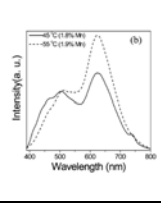
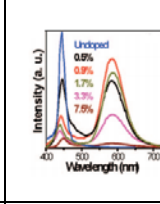
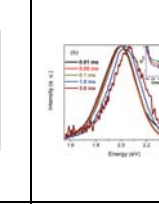
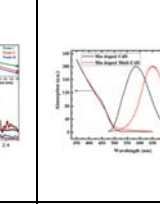
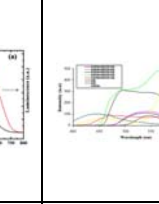
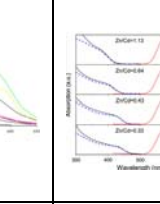
<sup>b</sup> *Institute of Materials, Ningbo University of Technology, Ningbo, 315016, People's Republic of China.*

<sup>c</sup> *School of Mechanical Engineering, Ningbo University of Technology, Ningbo, 315016, People's Republic of China.*

<sup>d</sup> *State Key Laboratory of Luminescence and Applications, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, People's Republic of China.*

<sup>e</sup> *School of Chemistry and Material Science, Guizhou Normal University, Guiyang 550001, People's Republic of China.*

**Table S1.** Typical works of Mn<sup>2+</sup> doped CdS or ZnCdS d-dots ever reported.

Spectra							
Quantum Efficiency	no mention	~ 2%	25%	no mention	no mention	no mention	29%
Synthesis Method	Reverse micelle method	Solvothermal/hydrothermal method	High-temp. organo-metal method	Solvothermal/hydrothermal method	High-temp. organo-metal method	One-pot aqueous route	High-temp. organo-metal method
References	<i>Adv. Mater.</i> <b>2006</b> , <i>18</i> , 1083-1085.	<i>Chem. Mater.</i> <b>2007</b> , <i>19</i> , 3252-3259.	<i>J. Am. Chem. Soc.</i> <b>2008</b> , <i>130</i> , 10605-10611.	<i>J. Phys. Chem. C</i> <b>2010</b> , <i>114</i> , 18323-18329.	<i>J. Am. Chem. Soc.</i> <b>2010</b> , <i>132</i> , 6618-6619.	<i>Spectrochim. Acta.</i> <b>2012</b> , <i>A93</i> , 70-74.	<i>Chem. Phys. Lett.</i> <b>2012</b> , <i>532</i> , 72-76.

### Calculation of the ZnS/CdS Layer Thicknesses

To calculate the amount of the precursors for shell growth, 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  $\text{MnSt}_2$  (0.05 mmol). Based on the precursor ratio ( $\text{ZnSt}_2:\text{MnSt}_2$ ) of 2:1 and the size of 2.8 nm detected by TEM for sample B, the radii of the MnS core can be estimated as:

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

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

Here,  $N$  is the number of the MnS nuclei in the reaction system,  $n_{\text{MnS}}$  is the mole amount of  $\text{Mn}^{2+}$  used in the reaction (0.05 mmol),  $r_{\text{MnS/ZnS}}$  is the radii of MnS/ZnS NCs (1.4 nm), which is coated by a thin ZnS layer with 0.06 g  $\text{ZnSt}_2$  precursor.  $D_{\text{ZnS}}$  and  $D_{\text{MnS}}$  are the bulk densities of ZnS and MnS (*i.e.* 4.1 and 4.0 g/cm<sup>2</sup>), respectively.  $M_{\text{ZnS}}$  and  $M_{\text{MnS}}$  are the molar mass of ZnS and MnS (*i.e.* 97.5 and 144.5 g/mol), respectively. Then the  $r_{\text{MnS}}$  is calculated to be 1.05 nm.

Therefore, the relation between the thickness (set as “X” monolayer) of the ZnS buffer (or CdS shell) layer and the mass amount of the zinc precursors ( $m_{\text{ZnSt}_2}$ ) (or the cadmium precursors ( $m_{\text{CdSt}_2}$ )) can be calculated via the following equations:

$$m_{\text{ZnSt}_2} = n_{\text{ZnS}} \times M_{\text{ZnSt}_2} = \frac{N \times V \times D_{\text{ZnS}}}{M_{\text{ZnS}}} \times M_{\text{ZnSt}_2} = \frac{N \times \frac{4}{3}\pi [(r_{\text{MnS}} + X \times d_{\text{ZnS}})^3 - r_{\text{MnS}}^3] \times D_{\text{ZnS}}}{M_{\text{ZnS}}} \times M_{\text{ZnSt}_2}$$

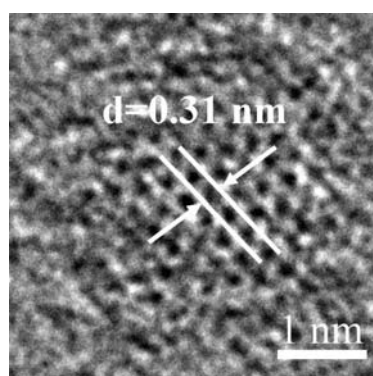
$$m_{\text{CdSt}_2} = n_{\text{CdS}} \times M_{\text{CdSt}_2} = \frac{N \times V \times D_{\text{CdS}}}{M_{\text{CdS}}} \times M_{\text{CdSt}_2} = \frac{N \times \frac{4}{3}\pi [(r_{\text{MnS/ZnS}} + X \times d_{\text{CdS}})^3 - r_{\text{MnS/ZnS}}^3] \times D_{\text{CdS}}}{M_{\text{CdS}}} \times M_{\text{CdSt}_2}$$

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

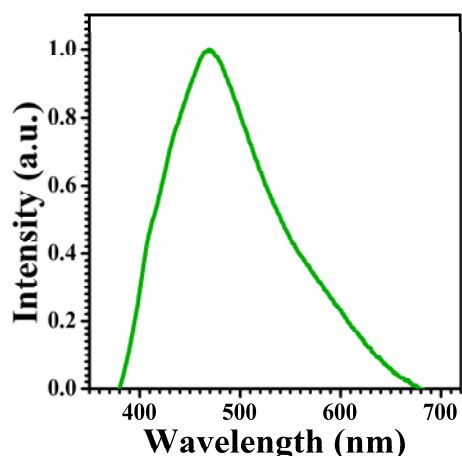
Here,  $N$  is the number of MnS nuclei in the reaction system,  $n_{\text{MnS}}$  is determined by the used MnSt<sub>2</sub> (0.05 mmol).  $r_{\text{MnS}}$  and  $r_{\text{MnS/ZnS}}$  are the radii of MnS (1.05 nm) and MnS/ZnS NCs (1.4 nm), respectively.  $D_{\text{ZnS}}$ ,  $D_{\text{CdS}}$  and  $D_{\text{MnS}}$  are the bulk density of ZnS, (4.1 g/cm<sup>3</sup>) CdS (4.8 g/cm<sup>3</sup>) and MnS (4.0 g/cm<sup>3</sup>), respectively.  $M_{\text{ZnS}}$ ,  $M_{\text{ZnSt}_2}$ ,  $M_{\text{CdS}}$ ,  $M_{\text{CdSt}_2}$ , and  $M_{\text{MnS}}$  refer to the molar mass of ZnS (97.5 g/mol), ZnSt<sub>2</sub> (631.5 g/mol), CdS (144.5 g/mol), CdSt<sub>2</sub> (679.5 g/mol), and MnS (87 g/mol), respectively.  $d_{\text{ZnS}}$  and  $d_{\text{CdS}}$  are the radii thickness of a monolayer (ML) of a ZnS (0.312 nm) and CdS (0.335 nm) layer, respectively. Then the calculation results of the ZnS/CdS layer thicknesses are listed in Table S2.

**Table S2.** The relation between the use of the mass amount of zinc (or cadmium) precursors and the ZnS (or CdS) layer thicknesses

ZnSt <sub>2</sub> /g	0.03	0.05	0.06	0.2	0.4
ZnS layers/ML	0.58	0.87	1.0	2.4	3.6
CdSt <sub>2</sub> /g	0.15	0.3	0.5		
CdS layers/ML	1.5	2.4	3.3		

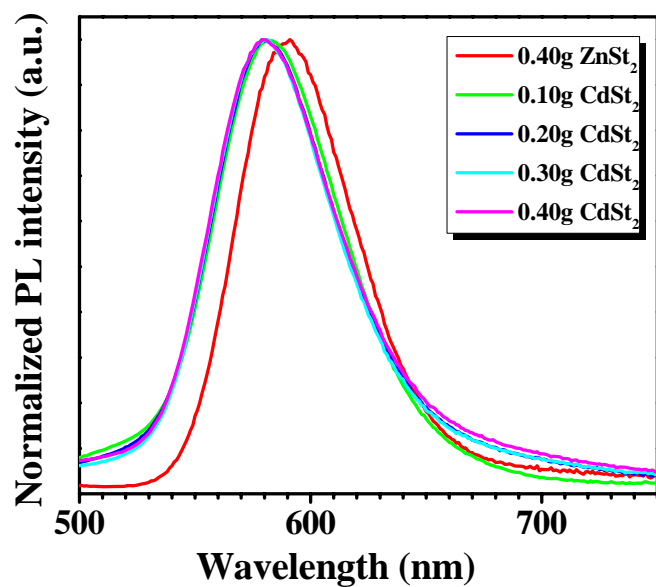


**Figure S1.** A typical HRTEM image recorded from Sample B.



**Figure S2.** The normalized PL spectrum of pure CdS nanoparticles, which is peaked at ~470 nm.

**(Typical Synthesis of CdS nanoparticles:** 0.06 g of CdSt<sub>2</sub> and 10 mL of ODE were loaded into a 50 mL three-neck flask, and degassed at 110 °C for 15 min by bubbling with argon followed by heating up to 240 °C. 2 mL of ODES stock solution (0.02 g S powders +2 mL ODE+0.4 mL OLA) were heated until the solution turned to be colorless, which was then injected into the above reaction flask at 240 °C. Immediately after the injection, the color of the solution was changed to be faint yellow, implying the formation of CdS nanoclusters. The fabricated CdS nanoparticles were purified repeatedly using methanol/hexanes and precipitated using acetone.)



**Figure S3.** PL spectra of MnS/ZnS and MnS/ZnS/CdS QDs with various amounts of cadmium precursors. The amount of the zinc precursor are 0.4 g ZnSt<sub>2</sub> (red line) for preparing MnS/ZnS QDs, further with 0.1 g CdSt<sub>2</sub> (green line), 0.2 g CdSt<sub>2</sub> (blue line), 0.3 g CdSt<sub>2</sub> (cyan line), and 0.4 g CdSt<sub>2</sub> (magenta line) for the growth of MnS/ZnS/CdS QDs, respectively. The MnS/ZnS/CdS and MnS/ZnS QDs are excited at 365 and 265 nm, respectively.

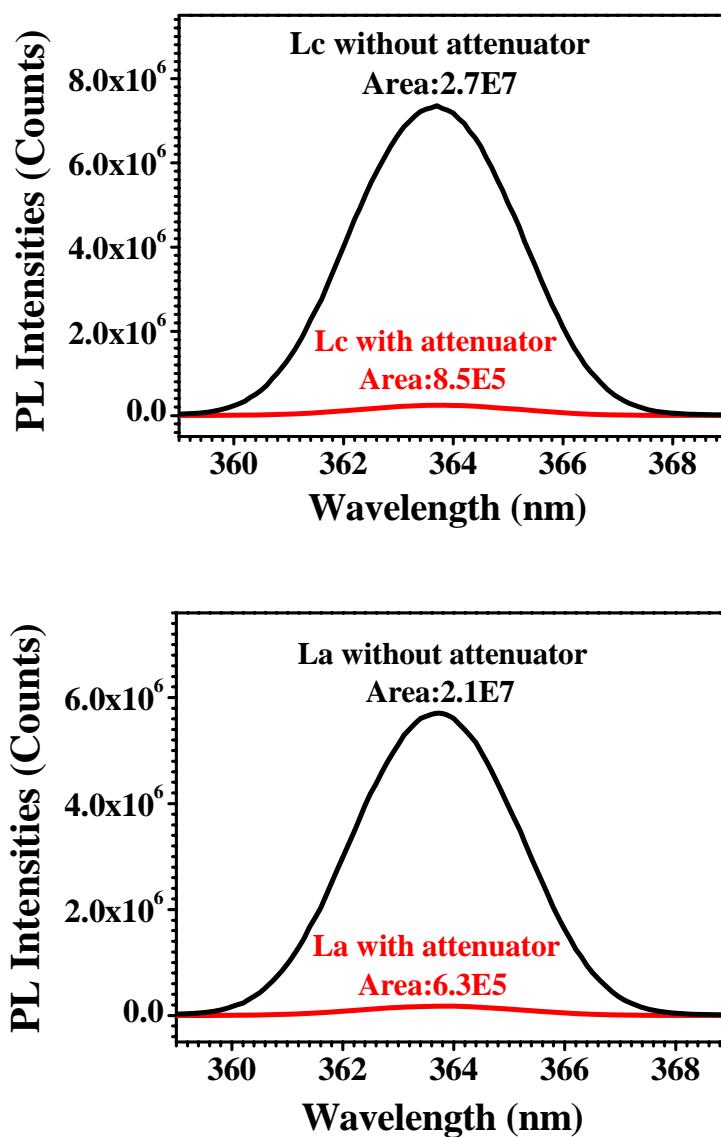
### ***The PL Quantum-Yield (QY) Measurements:***

The PL Quantum-Yield (QY) was recorded using a Horiba Jobin Yvon Fluoromax-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.

In order to adjust the Rayleigh excitation peak for the pure solvent to the desired count rate (suggested value  $\approx 10^6$  counts/s), the attenuator with a factor of  $\sim 32.3$  at the wavelength of 365 nm (as shown in Figure S4 ) 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 S5 and Figure S6, which were recorded from our typical experiments for the QY measurement of Sample E with different concentrations).



**Figure S4.** 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  $\sim 32.3$ .



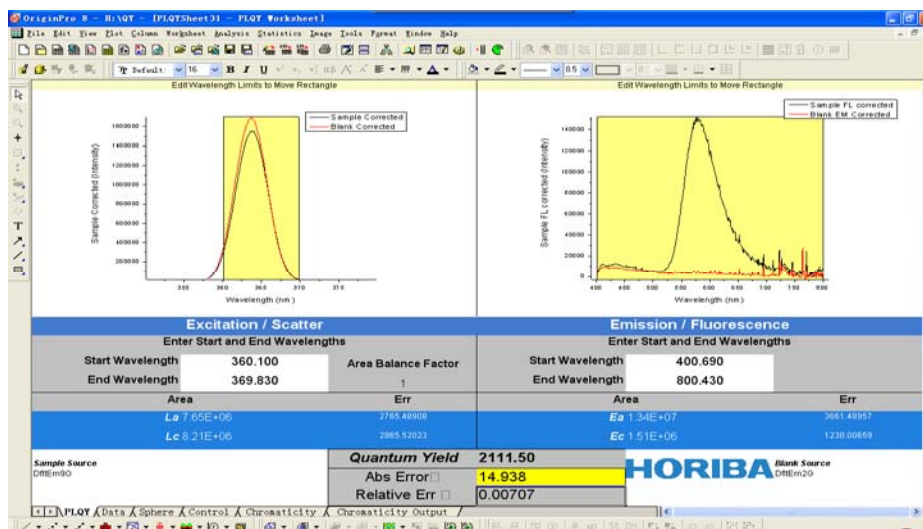


Figure S5. An original experimental data for the QY measurement of Sample E

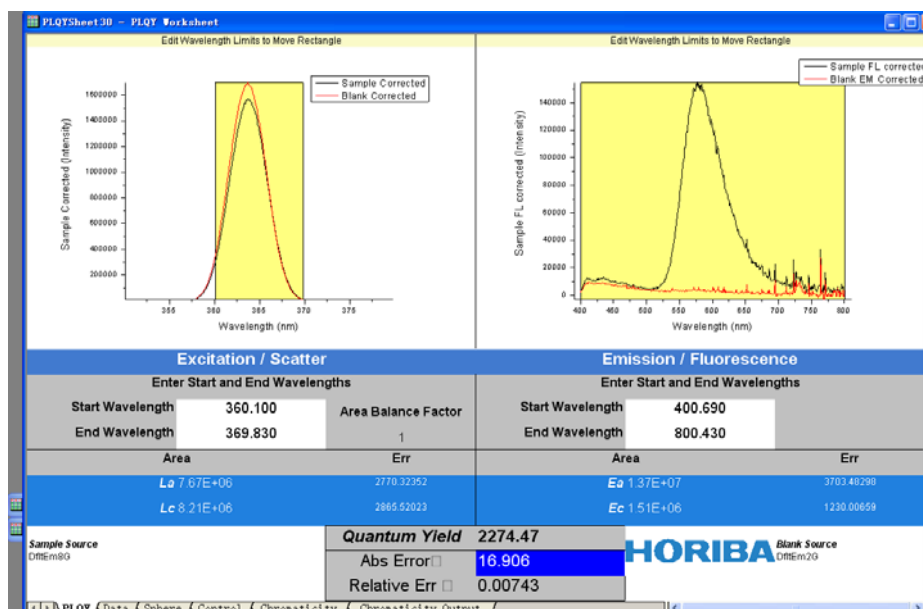


Figure S6. An original experimental data for the QY measurement of Sample E

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

$$QY_{(r)} = \frac{E_{a(r)} - E_{c(r)}}{L_{c(r)} - L_{a(r)}} = \frac{E_{a(m)} - E_{c(m)}}{(L_{c(m)} - L_{a(m)}) \times 32.3} = \overline{QY_{(m)}} / 32.3 = 2192 / 32.3 = 68$$

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  $\overline{QY_{(m)}}$  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.

### The PL decay and data fitting of MnS/ZnS/CdS QDs:

