Supplementary Information

Long-lived and Well-resolved Mn^{2+} Ion Emissions in CuInS-ZnS Quantum Dots

Sheng Cao[1,2], Chengming Li[1], Lin Wang[2], Minghui Shang[2], Guodong Wei[2], Jinju Zheng[2,], and Weiyou Yang[2,*]*

[1] School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, China.

[2] Institute of Materials, Ningbo University of Technology, Ningbo 315016, China.

[*] ***Corresponding Authors, E-mails:*** zhengzhao2007@163.com (J. Zheng) and weiyouyang@tsinghua.org.cn (W. Yang)

Tel: +86-574-87080966

Fax: +86-574-87081221

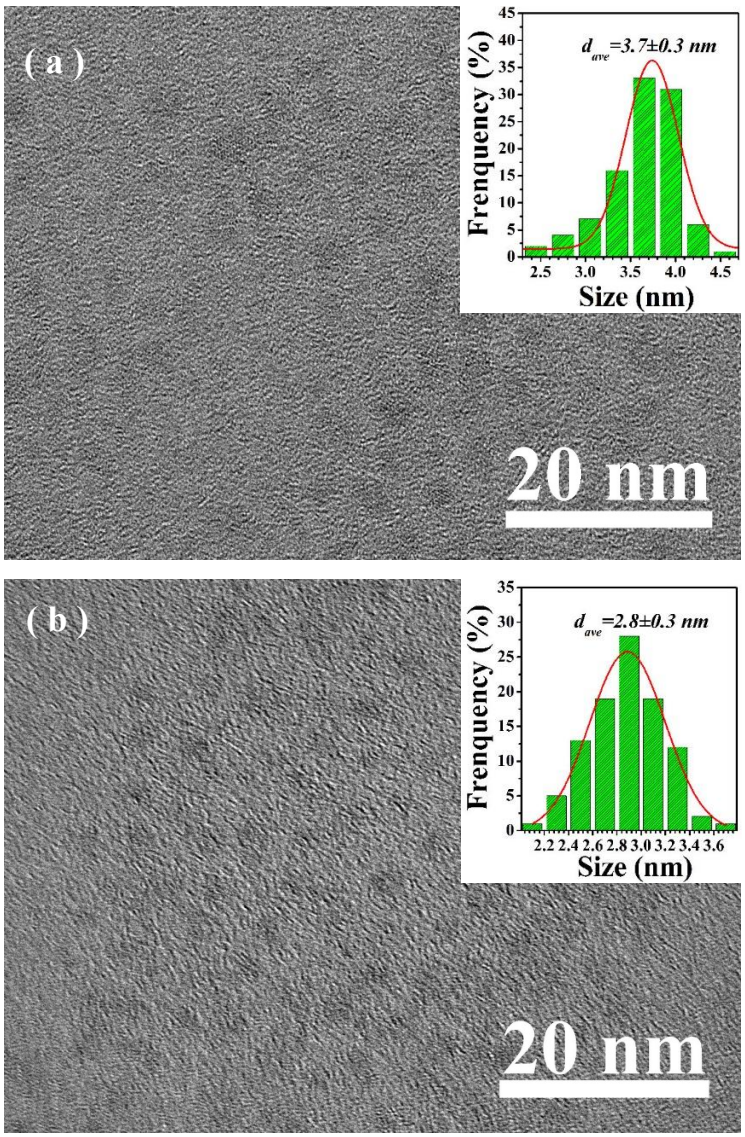
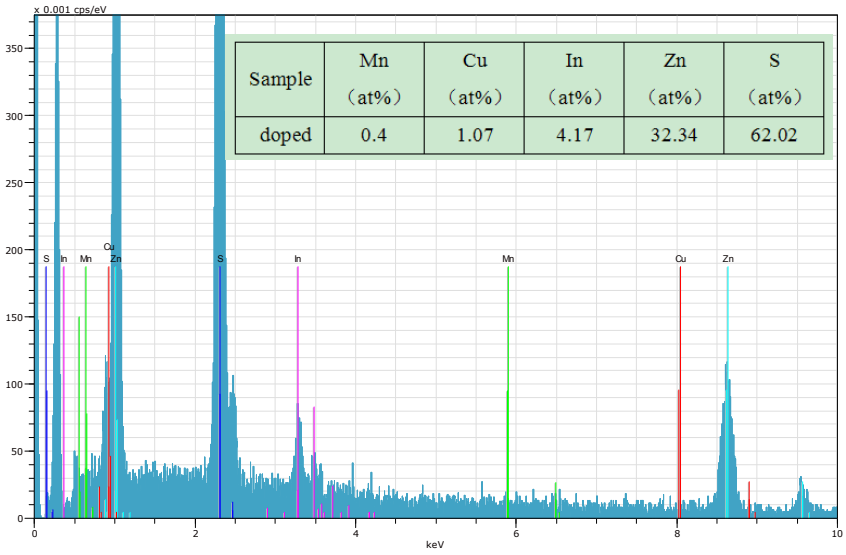


Figure S1 Typical TEM images and the corresponding size distributions (insets) of the Mn^{2+}-doped CIS-ZnS QDs (a) and CIS cores coated with a $Zn_{1-x}Mn_xS$ shells obtained after the second step in the hot-injection method (b). It should be pointed out that the pure CIS cores obtained after the first step in the hot-injection method are too small to be clearly detected by TEM.



Sample	Mn (at%)	Cu (at%)	In (at%)	Zn (at%)	S (at%)
doped	0.4	1.07	4.17	32.34	62.02

Figure S2 Typical EDX spectrum of Mn^{2+}-doped CIS-ZnS QDs. The inset shows the detailed chemical compositions.

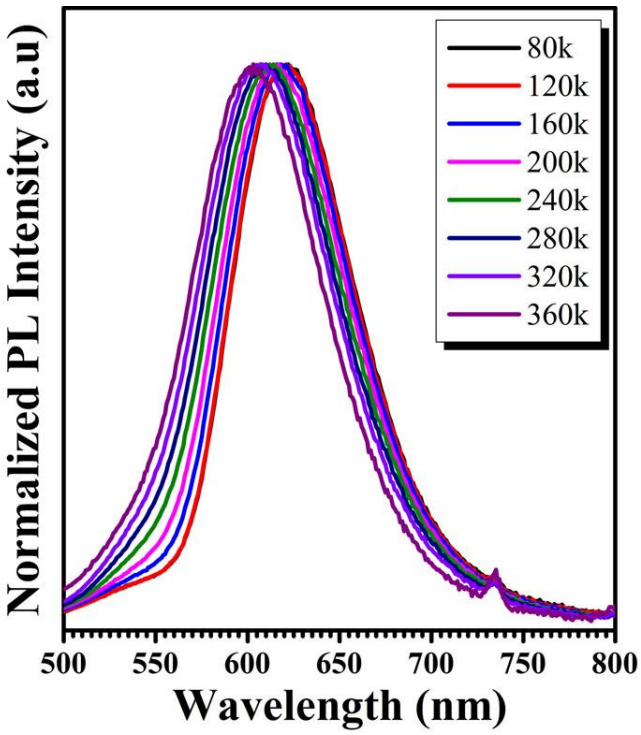


Figure S3 The normalized temperature-dependent PL spectra of Mn^{2+}-doped CIS-ZnS QDs recorded in the range from 80 to 360 K. The PL peaks are blue shifted systematically with the increase of temperatures, which is consistent with a typical emission of Mn^{2+} ion in II-VI semiconductor QDs due to its *d-d* transition

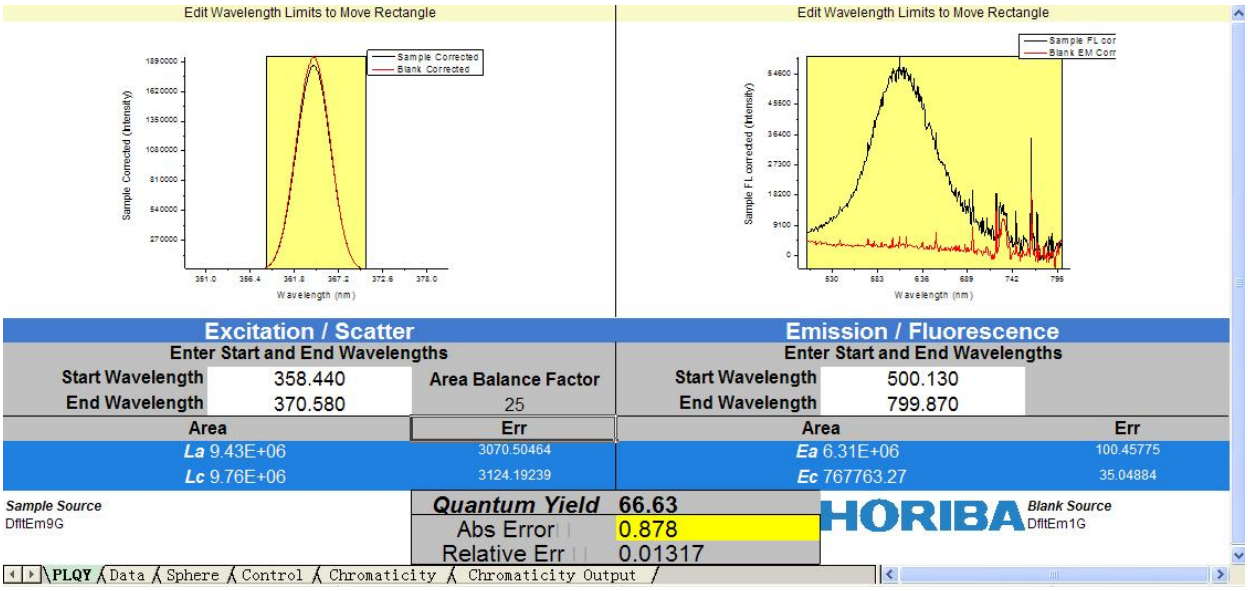


Figure S4 Details for the measurement on the PL QY of the Mn^{2+}-doped CIS-ZnS QDs. The Mn^{2+} ions dopant emissions in our QDs exhibit a QY up to 66%, which can be comparable to the best one of Mn^{2+}-doped semiconductor QDs ever reported.

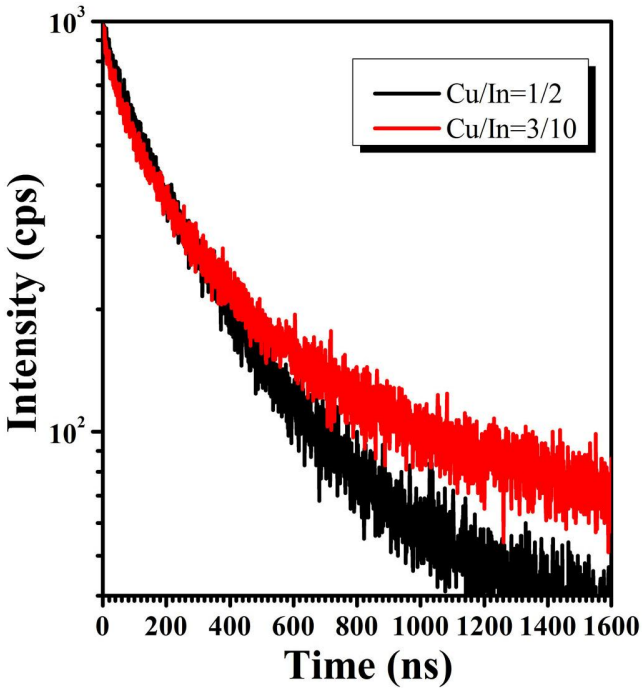


Figure S5 Typical decay curves of the Mn^{2+}-doped CIS-ZnS QDs at the Cu/In molar ratio of 1/2(black line) and 3/10(red line), respectively.

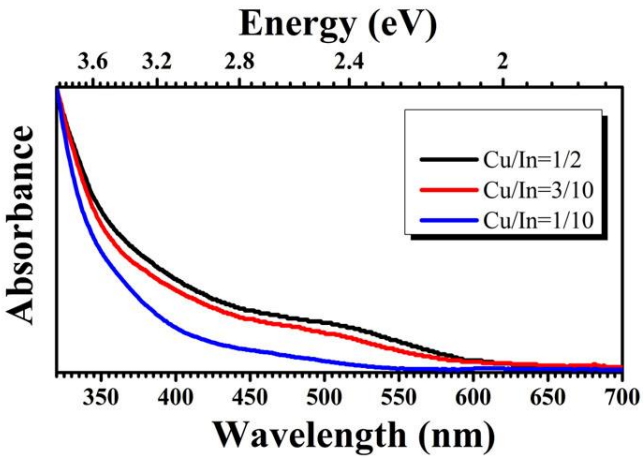


Figure S6 The representative UV-vis absorption spectra of Mn^{2+}-doped CIS-ZnS QDs at the Cu/In ratios of 1/2, 3/10 and 1/10, respectively. The absorption band edges show blue shifts with the decrease of the Cu/In ratios, indicating the corresponding increase of the bandgap energy.

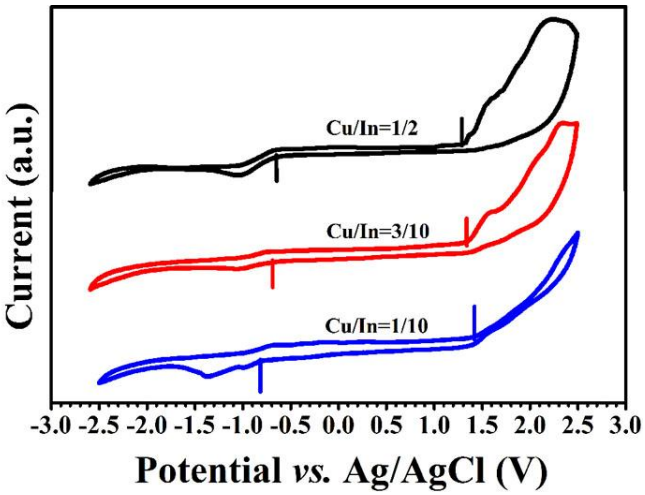


Figure S7 Typical cyclic voltammograms of Mn^{2+}-doped CIS-ZnS QDs at the Cu/In ratios of 1/2, 3/10 1/10, respectively. These experimental results imply that, with the decrease of Cu/In ratios, the absolute value of the onset oxidation potential (E_{ox}) and reduction potential (E_{red}) become larger, which indicates the increase of the bandgap energy, and consistent with the UV-vis absorption spectra.

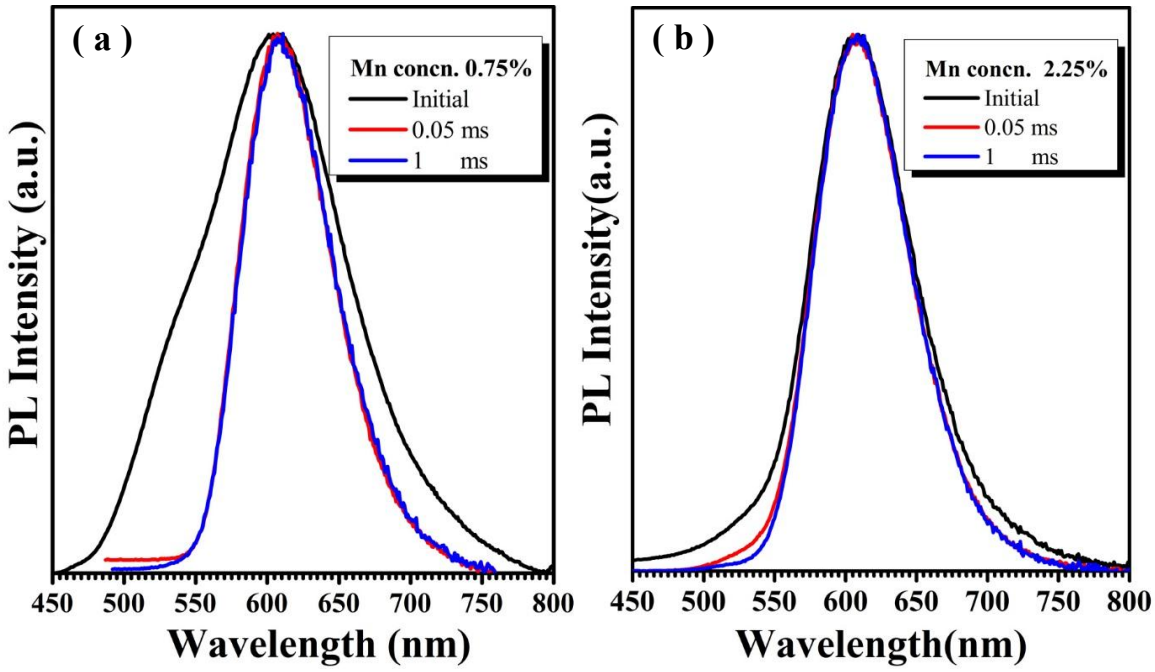


Figure S8 Normalized time-resolved PL spectra of Mn^{2+}-doped CIS-ZnS QDs with the nominal Mn^{2+} concentrations of 0.75% and 2.25%. The delay times are 0.05 ms (red lines) and 1 ms (blue lines), respectively, as compared to the initial emission.

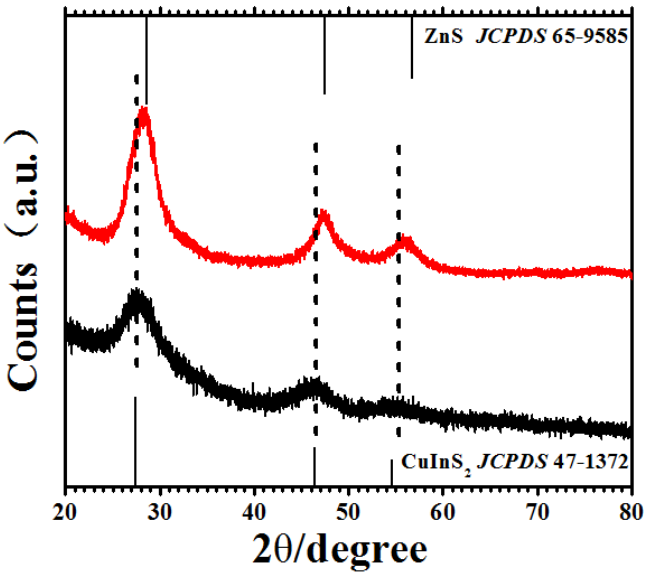


Figure S9 XRD patterns of the CIS cores coated with a $Zn_{1-x}Mn_xS$ shells (black) obtained after the second step in the hot-injection method and Mn^{2+}-doped CIS-ZnS QDs (red).

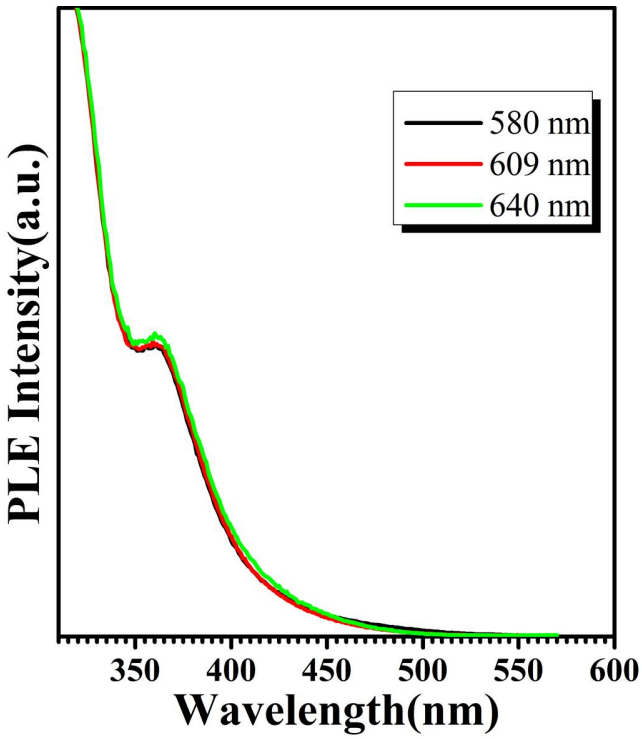


Figure S10 Normalized PLE spectra of Mn^{2+}-doped CuInS-ZnS QDs detected at different emission wavelengths, disclosing the homogeneous local environments of the emission centers.