Supplementary Information

Mn-doped ZnSe quantum dots initiated mild and rapid cation exchange for tailoring composition and optical properties of colloid nanocrystals: novel template, new applications

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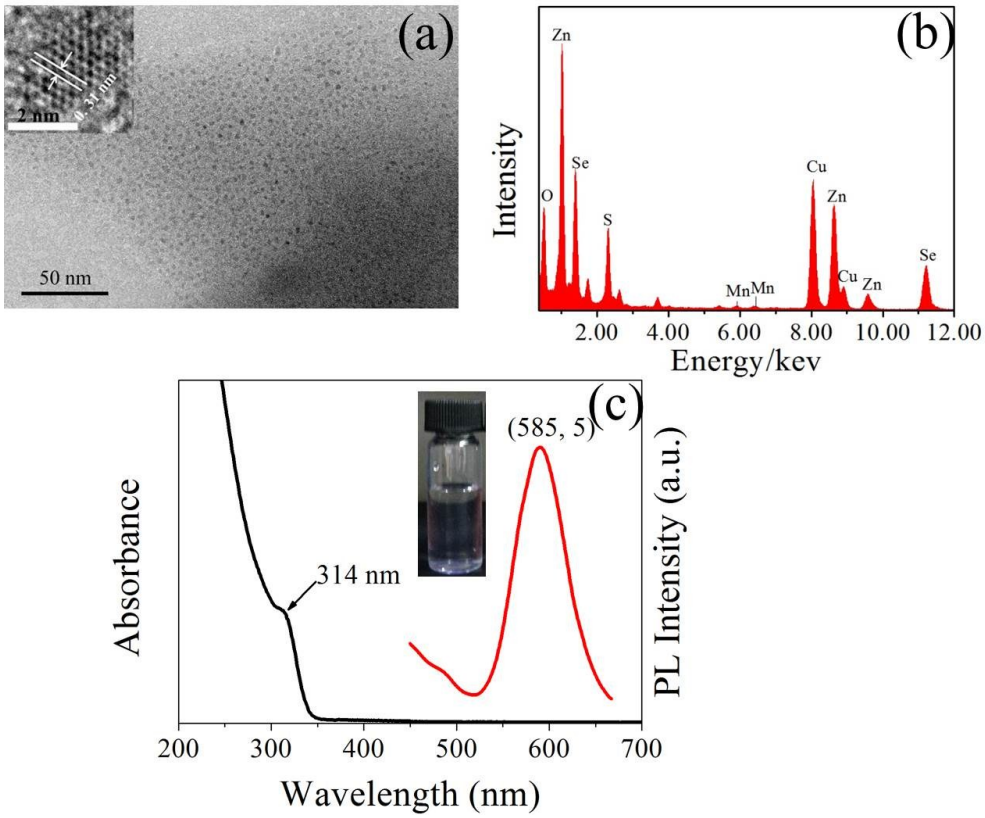

Fig. S1 Characterization of Mn-doped ZnSe QDs: (a) TEM image of Mn-doped ZnSe, a representative HRTEM is given as the inset. (b) EDX result of Mn-doped ZnSe QDs. (c) Fluorescence and absorbance spectra of Mn-doped ZnSe QDs, photo taken under the excitation of 365 nm is given as inset.

Fig. S1a depicts a transmission electron microscopy (TEM) image of D-dots prepared at pH = 8. The average size of the QDs was quantified from such images to be 2.7±0.5 nm. The inset of Fig. S1a shows the corresponding high resolution TEM (HRTEM) image. The distances between the adjacent lattice fringes were found to be 0.31 nm for Mn-doped ZnSe QDs, which is consistent with the literature value (0.324 nm) for the (111) *d* spacing (JCPDS No. 800021), meaning that the prepared doped (alloyed) QDs were in the cubic phase. Fluorescence (FL) and optical absorption spectra of the samples collected at pH = 8 are shown in Fig. S1b. The weak fluorescence peak at 585 nm is attributed to a $^4T_1 \rightarrow {}^6A_1$ transition of Mn^{2+} ions in T_d symmetry. The appearance of a characteristic peak indicates the successful introduction of Mn. The appearance of a Mn peak in energy dispersive X-ray (EDX) spectroscopy confirms the incorporation of Mn into the ZnSe lattice (Fig. S1c).

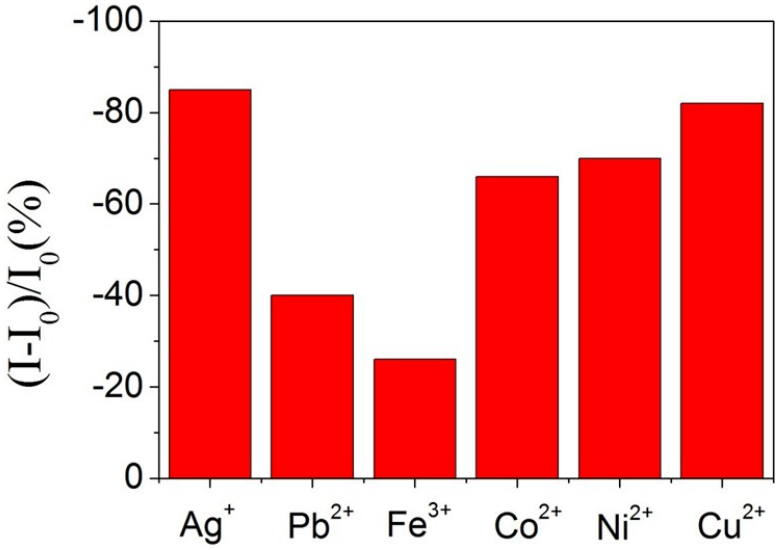

Fig. S2 The percentage of decrease in the fluorescence peak after incubating with 100 μM of common dopants (Ag^{+}, Pb^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+} and Cu^{2+}).

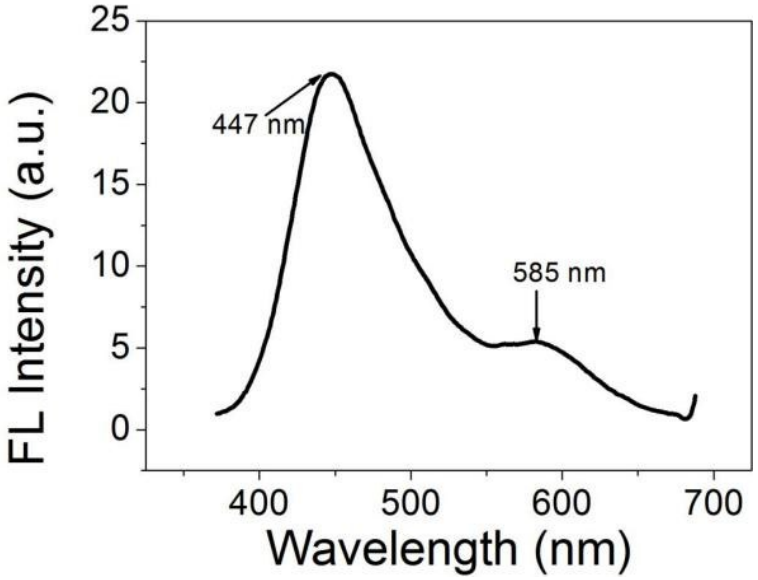

Fig. S3 PL spectra of Ag-doped ZnSe QDs after a 10 min reaction time.

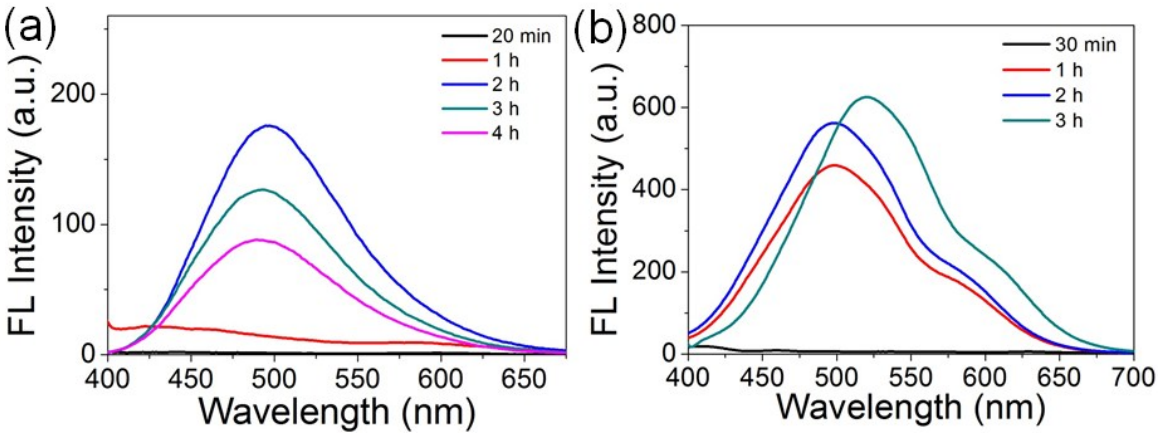

Fig. S4 PL spectra of Cu-doped ZnSe QDs (a) and Pb-doped ZnSe QDs (b) after different reaction times.

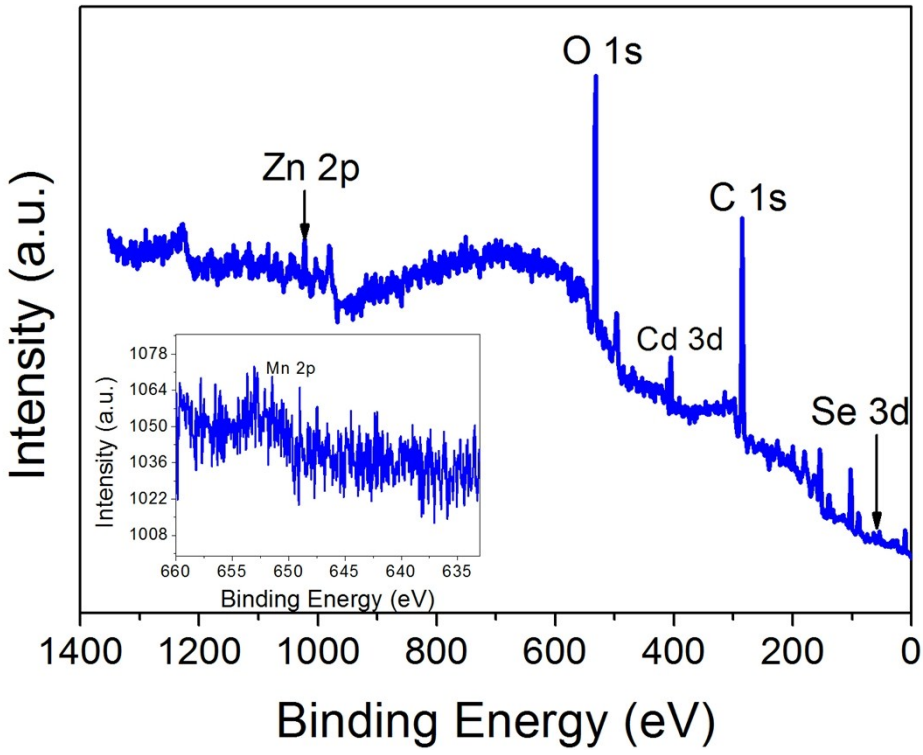

Fig. S5 XPS spectra of Mn-doped ZnSe QDs after incubating with 80 μM Cd^{2+} at 100 °C for 1 hour, the inset corresponds to the XPS Mn 2p spectrum.

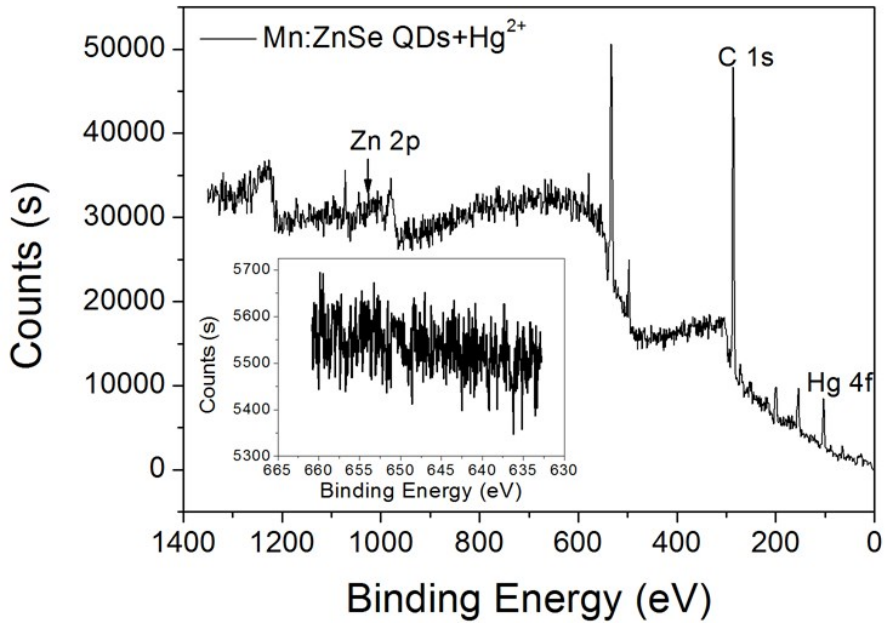

Fig. S6 XPS spectra of Mn-doped ZnSe QDs after the addition of 60μM Hg^{2+} at room temperature. The inset corresponds the Mn 2p spectra of Mn-doped ZnSe after cation exchange.

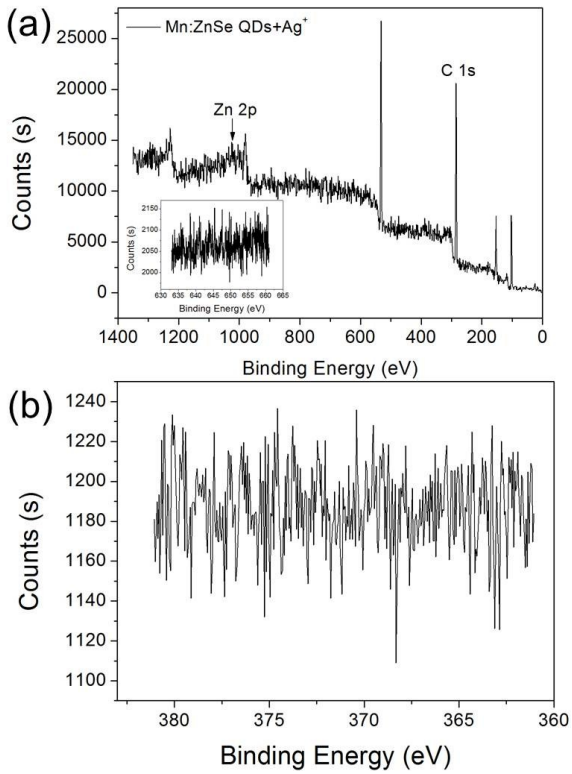

Fig. S7 XPS spectra of Mn-doped ZnSe QDs after the addition of 100 μM Ag^{+} at 50 °C. The inset corresponds the Ag 3d spectra of Mn-doped ZnSe after cation exchange.

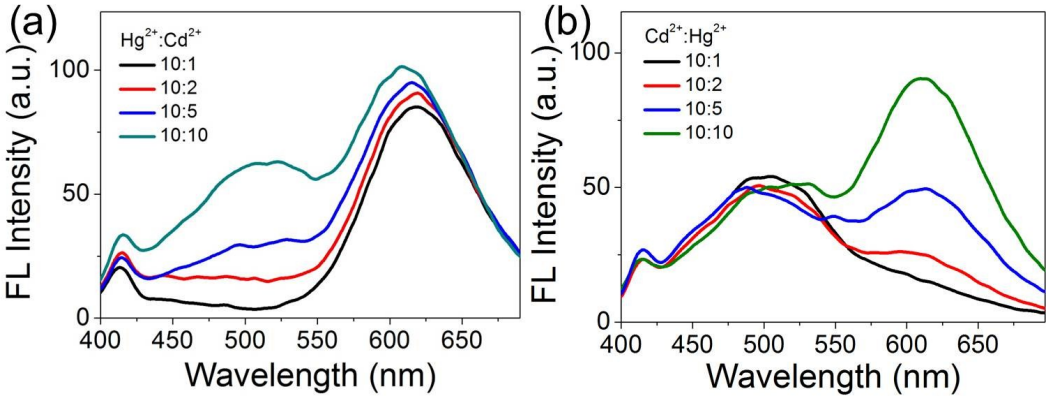

Fig. S8 Fluorescence spectra of Mn-doped ZnSe QDs in the presence of both Hg^{2+} and Cd^{2+}. (a) The molar ratio of Hg^{2+}/Cd^{2+} was set to 10:1, 10:2, 10:5 and 10:10, respectively. In every experiment, the concentration of Hg^{2+} was 10 μM. (b) The molar ratio of Cd^{2+}/Hg^{2+} was set to 10:1, 10:2, 10:5 and 10:10, respectively. In every experiment, the concentration of Cd^{2+} was 10 μM.

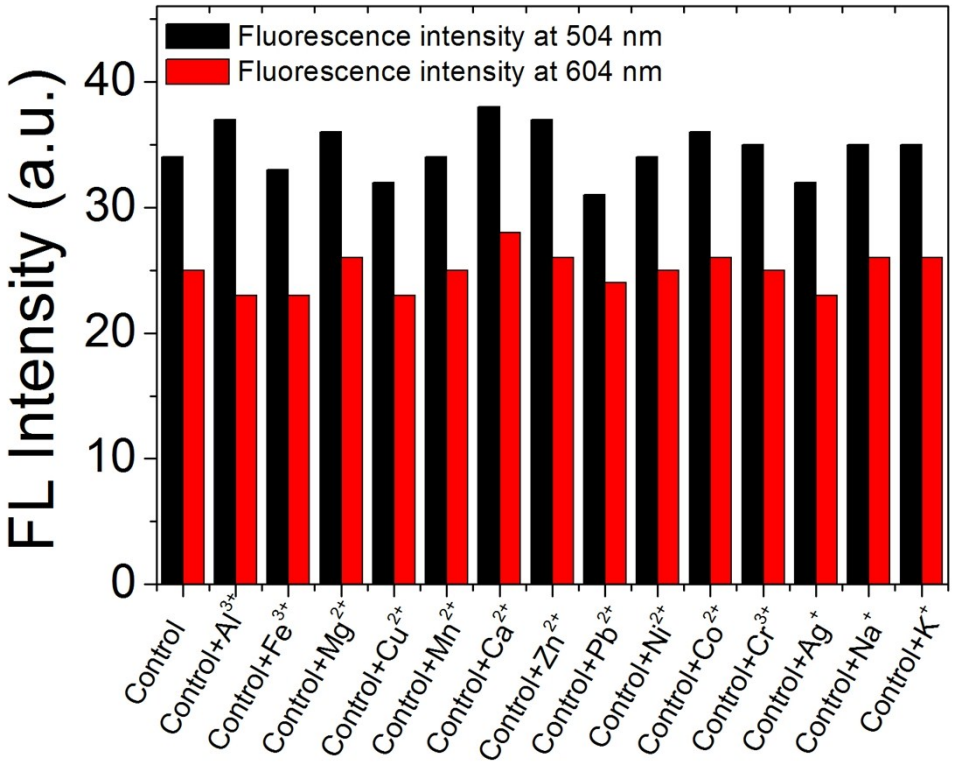

Fig. S9 Fluorescence intensity of Mn-doped ZnSe QDs with the addition of Cd^{2+}, Hg^{2+} and other metal ions. The control represents the addition of 5 μM Cd^{2+} and 2 μM Hg^{2+} into Mn-doped ZnSe QDs.

Table S1. References for the detection of different kinds of D-dots.

D-dots	Reference	Solvent
Cd-doped ZnSe QDs	Quinine Sulfate	0.1 M H_2SO_4
Hg-doped ZnSe QDs	Rhodamine 6G	Water
Ag-doped ZnSe QDs	Quinine Sulfate	Water
Cu-doped ZnSe QDs	Quinine Sulfate	Water
Pb-doped ZnSe QDs	Quinine Sulfate	Water

Table S2. Solubility product constants (K_{sp}) of different transition metal selenides at 25°C.

	K_{sp}		K_{sp}
ZnSe	3.6×10^{-26}	Ag_2Se	3×10^{-54}
CdSe	4×10^{-35}	CuSe	2×10^{-40}
HgSe	4×10^{-59}	PbSe	1×10^{-37}

Table S3 Changes in elemental content of Mn^{2+} and Ag^{+} after the addition of 100 μM Ag^{+} during different reaction duration.

Reaction Time	Mn^{2+} (%)	Ag^{+} (%)
10 min	2.0	0.0
1 h	0.8	1.6
4 h	0.2	5.2
7 h	0	14.0

Table S4 Calculated result of the concentration of Hg^{2+} and Cd^{2+} in samples using linear relationship of fluorescence intensity of Mn-doped ZnSe QDs and $C_{Hg}{}^{2+}$ ($C_{Cd}{}^{2+}$).

Samples	Added Hg^{2+} (μM)	Added Cd^{2+} (μM)	Calculated Hg^{2+} (μM)/Recovery[a]	Calculated Cd^{2+} (μM)/Recovery[a]
Hg^{2+}:Cd^{2+}				
10:1	10.00	1.00	9.57/95.7%	0.05/5%
10:2	10.00	2.00	9.86/98.6%	2.03/101.5%
10:5	10.00	5.00	9.64/96.4%	4.74/94.8%
10:10	10.00	10.00	10.10/101.0%	11.77/117.7%
Cd^{2+}:Hg^{2+}				
10:1	1.00	10.00	1.12/112.0%	10.15/101.5%
10:2	2.00	10.00	2.50/125.0%	9.15/91.5%
10:5	5.00	10.00	5.15/103.0%	8.67/86.7%
10:10	10.00	10.00	9.76/97.6%	9.38/93.8%