Supporting information:

Role of Redox Reaction and Electrostatics in Transition Metal Impurity-Promoted Photoluminescence Evolution of Water-Soluble ZnSe Nanocrystals [**]

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Figure S1 Low-magnification TEM image of ZnSe:Cu NCs.
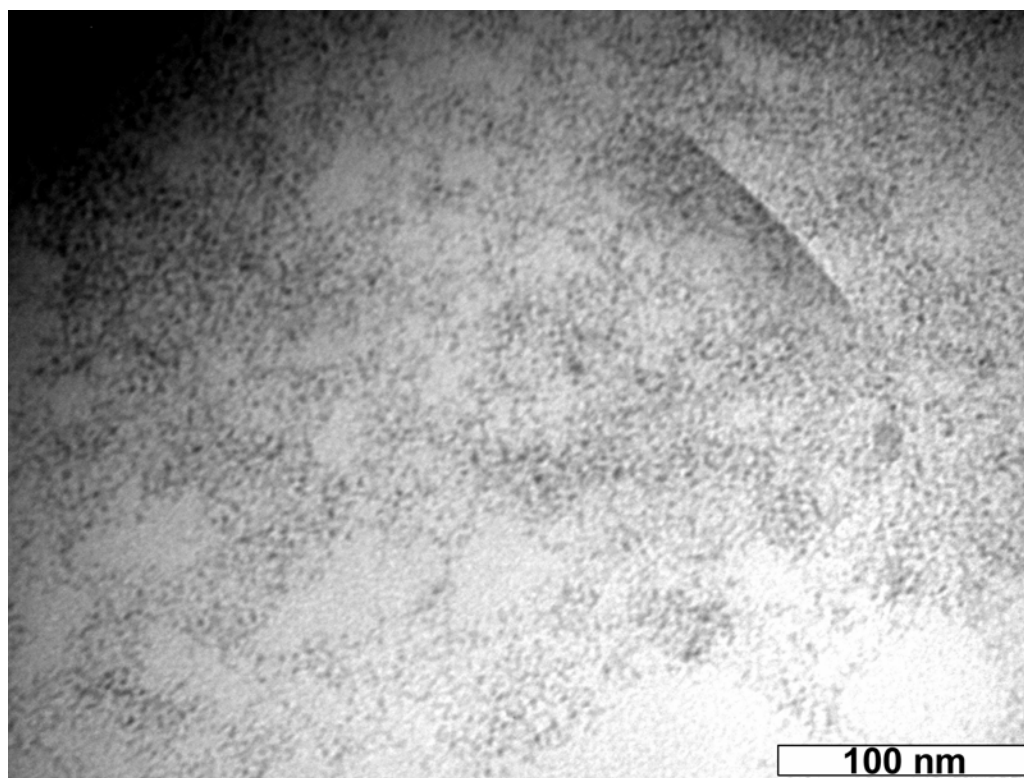
Figure S2 The XPS Mn 2p spectrum of ZnSe:Mn NCs. The Mn/Zn feed ratio was 0.02/1. The appearance of the characteristic Mn $2p_{3/2}$ peak at 641.4 eV and Mn $2p_{1/2}$ peak at 656.1 eV indicated the presence of Mn element in the resulting NCs.
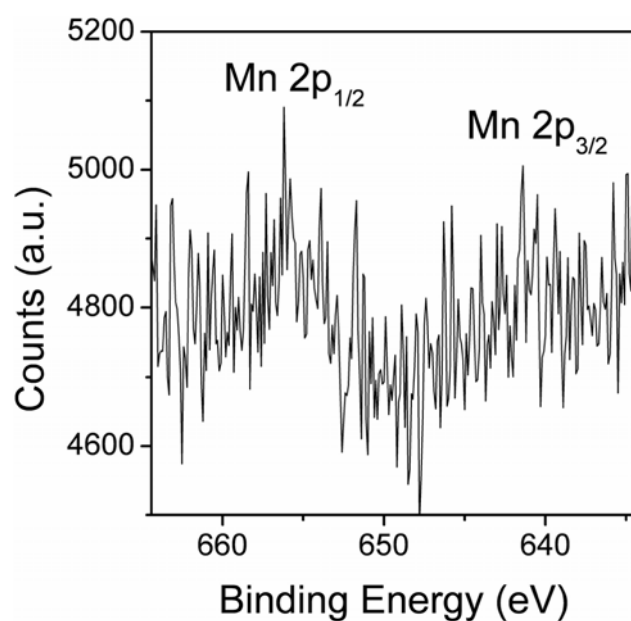
Figure S3 The schematic illustration of the PL emission levels of doped ZnSe NCs.
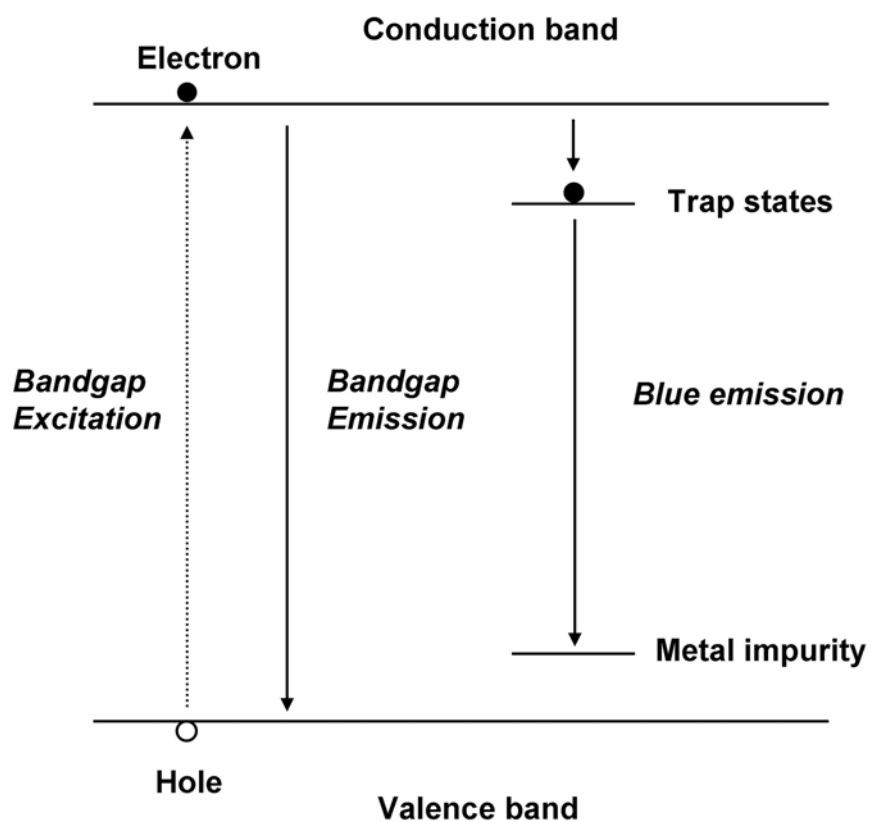

Figure S4 The schematic illustration of the surface adsorption and internal doping of copper in ZnSe NCs.
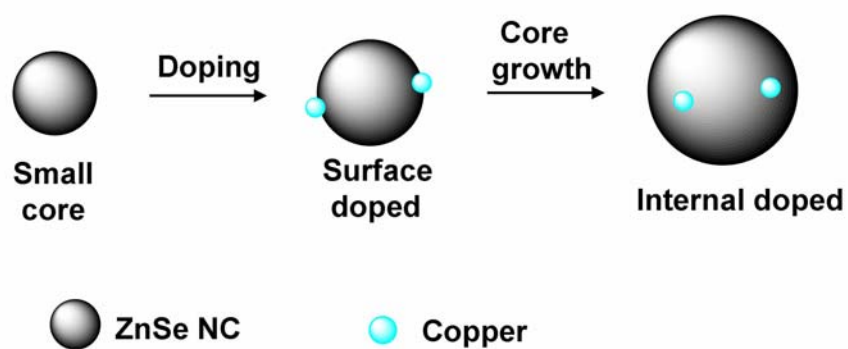
Figure S5 The schematic mechanism of the aggregation of Cu-doped ZnSe NCs.
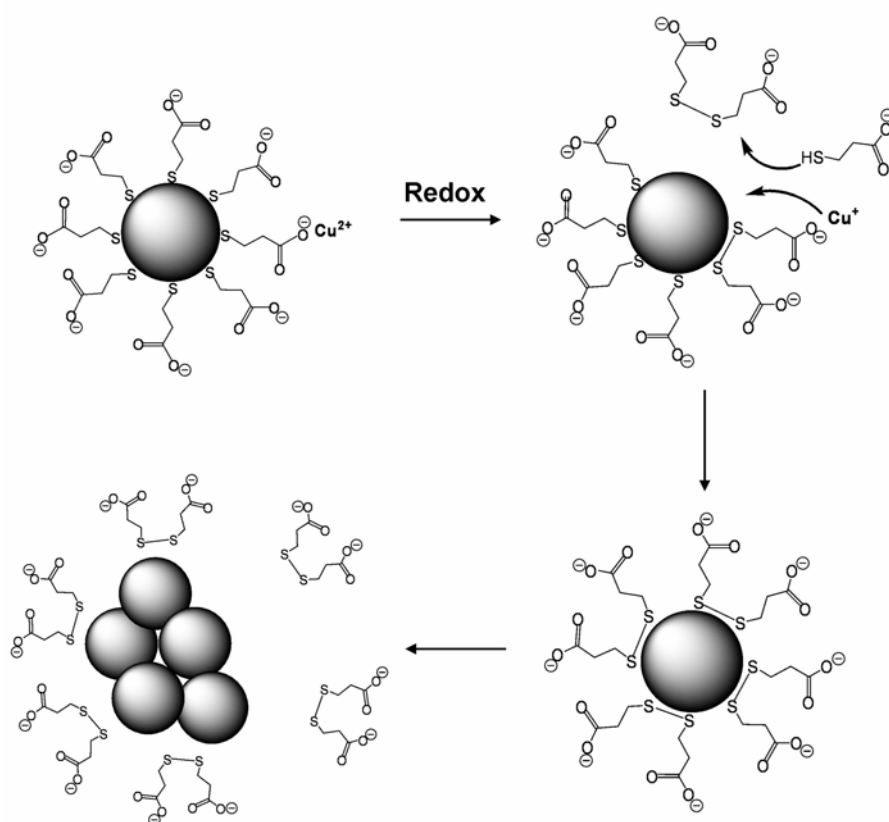
Figure S6 The comparison of $E_{Zn^{2+}/Zn}$ and E_{Cu^{2+}/Cu^+} in ZnSe:Cu-MPA system.

The computing method of the reduction potential of Zn^{2+}/Zn was expressed as

$$Zn^{2+} + 2e^- = Zn \qquad\qquad E^0_{Zn^{2+}/Zn} = -0.763 \text{ V}$$

$$Zn(MPA) + 2e^- = Zn + MPA^{2-} \qquad\qquad E^0_{Zn(MPA)/Zn} = E^0_{Zn^{2+}/Zn} - \frac{2.303RT}{nF}\lg K_{Zn(MPA)}$$

$$Zn(MPA)_2^{2-} + 2e^- = Zn + 2MPA^{2-} \qquad\qquad E^0_{Zn(MPA)_2^{2-}/Zn} = E^0_{Zn^{2+}/Zn} - \frac{2.303RT}{nF}\lg K_{Zn(MPA)_2^{2-}}$$

$$Zn(MPA)_3^{4+} + 2e^- = Zn + 3MPA^{2-} \qquad\qquad E^0_{Zn(MPA)_3^{4+}/Zn} = E^0_{Zn^{2+}/Zn} - \frac{2.303RT}{nF}\lg K_{Zn(MPA)_3^{4-}}$$

where R was the gas constant, T was the temperature, n was the number of transferred electron, F was the Faraday constant, which was 96500 $C \cdot mol^{-1}$, and K was represented to the stability constant. In our system, the pH value was 11.5, whereas Cu/Zn had a specific molar ratio. Consequently, Zn^{2+} existed the side reaction with OH^-, and MPA would react with H^+ and Cu^{2+}. In this context, α_{Zn} was the side reaction coefficient of Zn^{2+}, which was expressed as $\alpha_{Zn} = 1 + \sum_{i=1}^{4} \beta_i [OH^-]^i$, β_i was the cumulative stability constant, α_{MPA} was the side reaction coefficient of MPA, which was expressed as $\alpha_{MPA} = \alpha_{MPA(H)} + \alpha_{MPA(Cu)} - 1 = (1 + \frac{1}{K_{MPA}}) + (1 + K_{Cu(MPA)_y^{x-}}) - 1$, K_{MPA} was the ionization constant, and $K_{Cu(MPA)_y^{x-}}$ was the stability constant of Cu^{2+} and MPA.

So, take Zn(MPA) complex as the example, the reduction potential of Zn(MPA)/Zn was finally expressed as

$$E_{Zn(MPA)/Zn} = E^0_{Zn^{2+}/Zn} - \frac{2.303RT}{nF}\lg K_{Zn} + \frac{2.303RT}{nF}\lg \alpha_{Zn}\alpha_{MPA} + \frac{2.303RT}{nF}\lg \frac{[Zn(MPA)]}{[MPA^{2-}]}$$

The calculated value of $E_{Zn(MPA)/Zn}$ was approximately -0.840 V, which was slightly smaller than $E^0_{Zn^{2+}/Zn}$ (-0.763 V). Similarly, $E_{Zn(MPA)_2^{2-}/Zn}$ and $E_{Zn(MPA)_3^{4-}/Zn}$ were also calculated. We could also calculate $E_{Cu(MPA)/Cu^+}$ by using the aforementioned method. In

this context, Cu^{2+} would also react with OH^-, and MPA would react with H^+ and Zn^{2+}. In the end, the reduction potential of $Cu(MPA)/Cu^+$ was expressed as

$$E_{Cu(MPA)/Cu^+} = E^0_{Cu^{2+}/Cu^+} - \frac{2.303RT}{nF}\lg K_{Cu} + \frac{2.303RT}{nF}\lg \alpha_{Cu}\alpha_{MPA} + \frac{2.303RT}{nF}\lg \frac{[Cu(MPA)]}{[MPA^{2-}]}$$

The calculated $E_{Cu(MPA)/Cu^+}$ was approximately 0.848 V, which was quite larger than $E^0_{Cu^{2+}/Cu^+}$ (0.153 V). It meant in ZnSe:Cu-MPA system, the oxidability of Cu(II) was improved. Cu(II) was easier to be reduced by MPA than Zn(II).