

Supplementary Information

“Flash” synthesis of “giant” Mn-doped CdS/ZnS nanocrystals for high photostability

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Suppressed by Mn dopants, CdS's bandedge emitting of the Mn-doped CdS/ZnS (1 ML) NCs cannot be observed. Accordingly, we synthesized the undoped CdS NCs with the nearly same first exciton absorption (Abs) peak position at ~450 nm and the narrower size distribution, using hot-injection method, for “flash” synthesis. As shown in Fig. S1, there are significant blueshifts in both CdS's bandedge emitting and its first exciton Abs-peak after “flash” synthesis at the injection- and growth-temperature of 355 and 330 °C within 6 min. Factually, within the same time, a higher set temperature and a lower temperature drop contribute a greater blueshift.

Additionally, to some extent, the broad emission band at ~615 nm from undoped CdS NCs with the half high width of ~125 nm, is similar to the red band at ~615 nm from “flash” Mn-doped CdS/ZnS NCs with the half high width of ~75 nm. Thus the time resolved photoluminescence (PL) decays (as shown in the inset in Fig. S1) were monitored to differentiate them. The broad emission band from undoped CdS NCs with the PL lifetime of 0.48 microsecond (μs) in the scale of μs ,^{S1,S2} is attributed to the emission from surface traps of undoped CdS NCs. While the red emission band from “flash” Mn-doped CdS/ZnS NCs, with the PL lifetime of 2.19 millisecond (ms) in the scale of ms,^{S2,S3} is assigned to the emission from Mn^{2+} dopants (${}^4\text{T}_1$ to ${}^6\text{A}_1$). Furthermore, the broad emission band at around ~615 nm is not observed for the undoped CdS NCs with a 13 ML ZnS shell, because the ZnS capping,^{S4} combined with the subsequent thermal annealing,^{S5,S6} removes the surface traps.

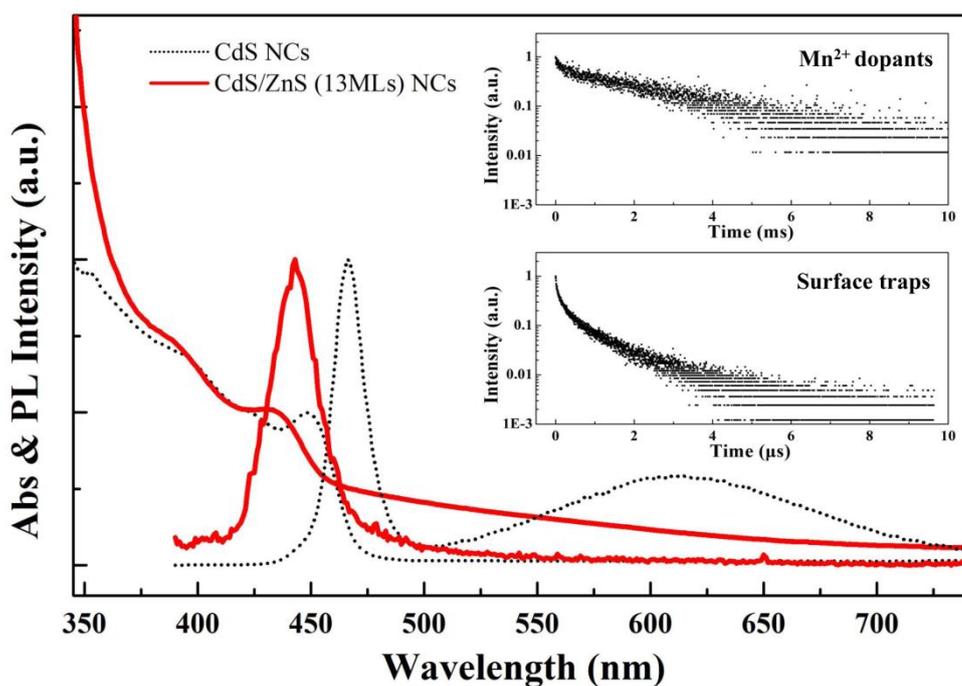


Fig. S1 Blushifts of Abs and PL spectra of undoped CdS and CdS/ZnS NCs. Inset: typical PL decay spectra of Mn^{2+} dopants in Mn-doped CdS/ZnS NCs (above) and surface traps in CdS NCs (below). The PL decay lines are fitted by a biexponential function to calculate the average lifetimes.

Fig. S2 shows X-ray diffraction (XRD) patterns and selected area electron diffraction (SAED) patterns (inset) of Mn-doped CdS/ZnS NCs before and after “flash” synthesis, with the ZnS shell thickness of 1 ML and 18 MLs, respectively. Both before and after “flash” synthesis, Mn-doped CdS/ZnS NCs mainly possess the cubic zinc blende structure. Calculated with the Scherrer equation, the lattice constant before and after “flash” synthesis is 5.8 and 5.4 nm respectively, corresponding to the lattice constant of CdS and ZnS bulk material, respectively. The presence of peak narrowing indicates that the crystallite size is increased, and the higher amplitude for the diffraction peak indicates that the crystallinity of NCs is improved by “flash” synthesis. The inset of Fig. S2 obviously shows that the SAED patterns of the NCs before (left) and after (right) “flash” synthesis are of zinc blende structure. More sharp patterns after “flash” synthesis indicate that both the crystallinity and crystallite size of the NCs are improved by “flash” synthesis; and a slight increase in the pattern’s diameter demonstrates a decrease in lattice constant of the NCs. In a word, it can be concluded, from both XRD and SAED patterns, that Mn-doped CdS/ZnS NCs

with zinc blende structure have a decrease in lattice constant but an increase in both crystallinity and crystallite size during “flash” synthesis.

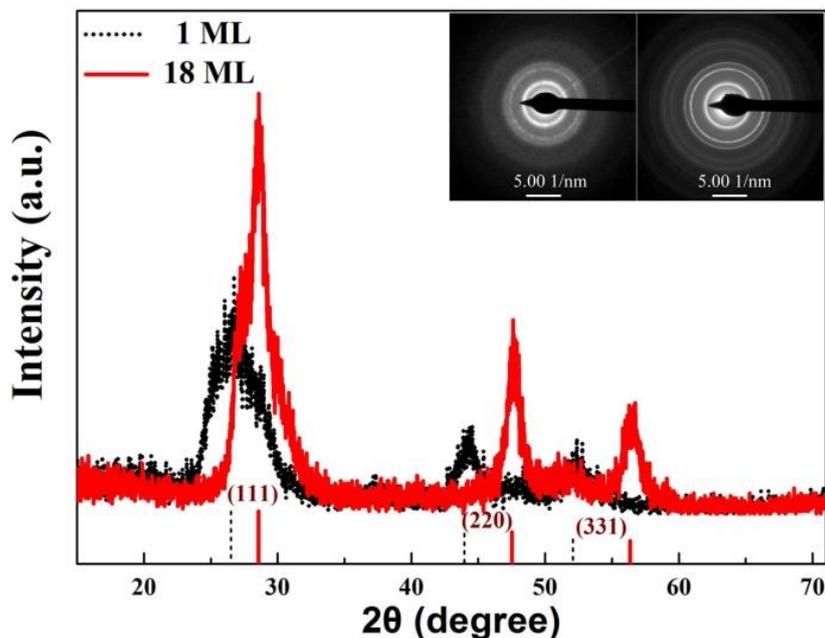


Fig. S2 XRD patterns and SAED patterns (inset) of Mn-doped CdS/ZnS NCs before and after “flash” synthesis.

References

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