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Modulating Charge-Carrier Dynamics in Mn-Doped All-Inorganic Halide Perovskite Quantum Dots through the Doping-Induced Deep Trap States

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ABSTRACT: Transition-metal ion doping has been demonstrated to be effective for tuning the photoluminescence properties of perovskite quantum dots (QDs). However, it would inevitably introduce defects in the lattice. As the Mn concentration increases, the Mn dopant photoluminescence quantum yield (PLQY) first increases and then decreases. Herein, the influence of the dopant and the defect states on the photophysics in Mn-doped CsPbCl$_3$ QDs was studied by time-resolved spectroscopies, whereas the energy levels of the possible defect states were analyzed by density functional theory calculations. We reveal the formation of deep interstitials defects (Cli) by Mn$^{2+}$ doping. The depopulation of initial QD exciton states was studied by time-resolved spectroscopies, whereas the energy levels of the possible defect states were analyzed by density functional theory calculations. We reveal the formation of deep interstitials defects (Cli) by Mn$^{2+}$ doping. The depopulation of initial QD exciton states is a competition between exciton–dopant energy transfer and defect trapping on an early time scale (<100 ps), which determines the final PLQY of the QDs. The present work establishes a robust material optimization guideline for all of the emerging applications where a high PLQY is essential.

Doping Mn$^{2+}$ ions into the lattice of quantum dots (QDs) has attracted extensive attention because it creates stable sub-band-gap Mn$^{2+}$ d–d emission ($^{4}T_1$–$^{6}A_1$) with an extremely long lifetime. This property broadens the scope of the optoelectronic application of these QDs. Because the Mn$^{2+}$ d–d emission is triggered by the energy transfer (ET) from the QDs after photoexcitation, selecting host QDs with a suitable optical band gap and a high photoluminescence quantum yield (PLQY) is essential. Doping Mn$^{2+}$ in conventional II–VI semiconductors QDs is feasible, but the PL of the QDs themselves is restricted by the sub-band-gap defect states. On the contrary, the highly ionic lattice of all inorganic cesium lead halide (CsPbX$_3$) perovskite QDs renders these nanomaterials highly tolerant to defects with a much higher PLQY compared with the II–VI QDs. In addition, Mn$^{2+}$ and Pb$^{2+}$ have similar ionic radii and comparable bond dissociation energies toward halide ions. Therefore, doping Mn$^{2+}$ ions in perovskite QDs has recently been widely investigated. However, the reported PLQY of the Mn$^{2+}$ d–d emission in doped QDs is below expectations. This raises important questions regarding the dynamics of the excitons and charge carriers after the excitation of host QDs and their correlations with the dopants. Previous research focused on the exciton–dopant ET process without considering any influence from the defect trapping. Recent studies put forward a trap-mediated exciton–dopant ET model where initially excited charge carries would first be localized in a shallow trap before they could migrate to the Mn$^{2+}$ states. However, the origin and energy alignment of such a trap state versus a dopant state remain unjustified. In addition, doping metal ions could generate deep defects in the lattice to quench the PL emission, which may more greatly affect the final PLQY of the doped QDs.

In this contribution, we first confirm the major internal trap states in Mn-doped CsPbCl$_3$ QDs to be the doping-induced interstitials Cl, via density functional theory (DFT) calculations. Such defect states locate deep within the Mn$^{2+}$ orbitals. The charge-carrier trapping as well as the exciton–Mn ET dynamics with various doping concentrations are then analyzed using transient absorption (TA) and time-resolved photoluminescence (TRPL) spectroscopies. We conclude that exciton–Mn ET occurs within tens of picoseconds, with the transfer rate first increasing and then decreasing with the increase in Mn dopants. Concurrently, hole trapping at the doping-induced Cl states happens at ~83 ps. Instead of mediating exciton–dopant ET, such deep trap states mainly quench the intrinsic emission from the QDs, which competes...
with the ET process. Such competition determines the overall PLQY of the dual emission in QDs. This work provides a novel foundation for understanding the photophysics of transition-metal-doped perovskites QDs.

The Mn-doped CsPbCl₃ QDs were prepared by the reported hot-injection methods. For details, see the Experimental Section in the SI.) Figure 1a,b shows the morphology and the structure of the doped QDs. The TEM images in Figure S1 indicate that Mn doping could slightly shrink the crystal size of QDs from 8.6 to 7.3 nm, probably due to the higher formation energy of undoped QDs confirmed in the following calculations, which reduces the critical particle size during the Ostwald ripening. The Mn concentrations in the lattice derived from coupled plasma mass spectroscopy (ICP-MS) are about 0, 0.1, 0.2, 0.6, 1.8, and 38% with the increasing MnCl₂ precursor concentration. (See Table S1 for the feeding ratio.) Figure 1c illustrates the absorption and emission spectra of undoped and doped QDs. The absorption band edge of all QDs is ~405 nm, corresponding to an optical band gap (E_g) of 3.06 eV regardless of the doping level. No obvious dopant-related absorption band can be observed due to the spin-forbidden d–d transition of the Mn²⁺ dopant states (4T₁−4A₂). The doped QDs exhibit an extra broad Mn²⁺ d–d emission band at ~600 nm, in addition to the narrow exciton emission at ~405 nm. Figure 1d and Table S2 illustrate the evolution of the PLQY for these two types of emission with the increasing doping level. The band-edge exciton PLQY decreases monotonously, whereas the Mn²⁺ emission QY first increases and then decreases with the maximal QY at a Mn concentration of 0.6%. Consequently, the overall PLQYs of the QDs follow the same trend as those of the Mn²⁺ emission. The PLQY change should directly correlate with the rates between the radiative and nonradiative recombinations of photogenerated charge carriers. For conventional QDs, it is generally interpreted by the diminishing/introduction of the defect states. However, in our case, the QD–Mn ET also contributes to depopulating the initial photoexcited charge carriers in the host QDs, which complicates the scenario. Here we first analyze the possible condition of doping-induced defects via structure characterization. TEM studies confirm the absence of long-range-order lattice changes after doping (cf. Figures S2 and S3). The electron paramagnetic resonance (EPR) measurement of the as-obtained QDs (Figure 1e) and QDs under various conditions (Figure 1f) demonstrates that Mn²⁺ ions occupy Pb²⁺ sites with an octahedral ligand field and uniform distribution in the lattice. The Mn d orbital resides within the Mn²⁺ dopant states (4T₁−4A₂). The calculated E_g from the valence band maximum (VBM) to the conduction band minimum (CBM) of undoped CsPbCl₃ is ~2.5 eV (Figure 2), which is naturally smaller than the experimental values when using the PBE exchange-correlation functional. The CBM and VBM are dominantly contributed by Pb and Cl orbitals, respectively (Figure S6). The Mn d orbital resides within the E_g with the d–d transition energy around 2.0 eV, which is consistent with the Mn²⁺ emission energy observed in the PL spectra. In the next step, all of the possible point defects in the Mn-doped lattice, namely, vacancies (Mn−V_Cs, Mn−V_Pb, and Mn−V_Cl), interstitials (Mn−Csi, Mn−Pbi, and Mn−Cl), and antisites (Mn−CsiPb, Mn−CsiCl, Mn−Pbi, Mn−PbiCl, Mn−CsiCl, and Mn−Cl) were simulated. The intrinsic point defects in undoped QDs were also evaluated as a reference. (For a detailed methodology, see the SI.) The energy configurations of the calculated VBM/CBM and the Mn²⁺ states in the presence of all types of defect states for undoped and doped QDs are summarized in Figure 2a,b, with the corresponding formation energy of each defect listed in Tables S3 and S4, respectively. Here three conditions proved by experiment should be simultaneously fulfilled to determine which defects can be valid: (1) Mn²⁺ states should locate within the E_g; (2) the E_g of the host QDs and the energy gap of the Mn²⁺ d–d states should stay unchanged when defects are induced, as evidenced by the absorption and PL results; and (3) the formation energy of such a defect should be low. Three points (A, B, and C in Figure 2c) representing various Cl compositions were chosen to evaluate the formation energy density of available equilibrated chemical potential region for CsPbCl₃. Here the dominating defect states, PbCs, in near CsPbCl₃ are much easier to generate with lower formation energy as well as shallower energy
compared with the previously reported V Cl in the same system. On the contrary, Mn2+ doping induces new possible defects, Cl interstitials (Cli). According to the energy level alignment, the PbCs in neat QDs tend to trap electrons, and Cli in doped QDs are more likely to trap the holes. These defects are all generated by the displacement of the Pb ions from the \[\text{[PbCl}_6\]^{4-}\] octahedra toward the A cation sites after the partial substitution of Pb2+ ions with Mn2+ ions, as illustrated in Figure 2d.

The above structural analysis suggests diminished intrinsic shallow traps together with the formation of deep hole traps in the CsPbCl3 lattice owing to the Mn2+ doping. TA was then used to explore the impact of doping on the charge-carrier dynamics (Figure 3 and Figures S10 and S11). The TA spectra of all samples show characteristic band-edge ground-state bleach (GSB) at \(\sim 400\) nm due to the band-edge-state filling. The singular value decomposition (SVD) fitting of the spectra resolves four main components in undoped QDs with lifetimes of 3.2 ps, 38 ps, 540 ps, and 15 ns (Figure 3a). The spectral features for all components reflect the depopulation of the band-edge excited states. Any high-order Auger processes can first be excluded due to the low excitation intensity with excitation density per QD, \(<N>\ll 1\). (See the SI for details.)

The lifetime of the longest component is similar to the slow decay component in the TRPL kinetics of undoped QDs (7.3 ns, Figure S12) and therefore should be assigned to the radiative recombination. The other three components should then be related to the nonradiative recombination of the excited charge carriers. In doped QDs, four main spectral components can still be fitted but with shorter lifetimes, as shown in Figure 3b (i.e., 3.2 ps, 20 ps, 540 ps, and 6.5 ns). The GSB recovery kinetics in Figure 3c further demonstrates the faster excited-state depopulation in doped QDs with extra charge-carrier recombination pathways. Previous reports have directly compared the GSB kinetics in doped and undoped QDs and extracted the dopant−Mn ET time to be 380 ps. However, additional trapping processes are introduced via Mn doping, as previously discussed. Here we can probe the rising edge of the ps-TRPL kinetics for the Mn2+ emission in doped QDs to unambiguously assign the dopant−Mn ET dynamics (Figure 4a). The time constants for the rising first decreases and then increases with the increasing Mn concentration, as illustrated in Figure 4a. Such a trend also resembles the early time dynamics of TA GSB decays in Figure 3c. As summarized in Table S5, the lifetimes of two TA spectral components, \(\tau_1 = 3.2\) ps and \(\tau_1 = 540\) ps, are similar for the undoped and the doped samples regardless of the doping level. We propose that these concurrent components represent the same surface trapping pathways where the excited electrons get trapped within 3.2 ps and then relax to ground state in 540 ps. Such trapping only occurs within a part of the QDs overwhelming other recombination processes in those dots. Otherwise, the trapping would quench the emission from all QDs. This surface-trapping process should also be insensitive to the internal defects induced by the doping. Such fast surface trapping within picoseconds is also observed in conventional CdSe QDs. The spectral features of the second components are identical for undoped and all doped QDs.
implying the similar excited species. The lack of positive excited-state absorption after the band-edge bleach (410 nm) indicates the absence of an excitonic Stark shift and therefore should be assigned to the transfer of dissociated free charge carriers. Their rate constants \( k_1 \) change with the doping level, following the same trend as the ET rates, \( k_{ET} \), extracted from TRPL but with higher values, as depicted in Figure 4c. We noticed that such "delayed" building up of the Mn2+ emission has been observed and explained by other groups using the shallow trap-state intermediated ET model5,25 However, on the basis of our theoretical calculation, the Cl trap states reside well above the Mn \(^{6}A_1\) orbital by 0.45 eV (Figure 2b), which is much larger than the thermal energy. This means that the detrapping of the localized holes at the trap states to Mn2+ states is unlikely. Instead, the trapped hole tends to relax to the ground state, serving as an additional nonradiative recombination pathway. Therefore, the overall excited-state depopulation dynamics in the pool of QDs with QD \( \rightarrow \) Mn ET can be expressed by the three-level system (Figure 3d), whereas the TA decay rate \( k_1 \) is composed of the nonradiative recombination rate, \( k_{NR} \), and the \( k_{ET} \). For a detailed explanation, see the SI.) This is consistent with the observation in Figure 4c. We can extract a nonradiative recombination rate related to hole trapping, \( k_{NR} \approx k_1 - k_{ET} \), to be \( \sim 0.012 \text{ ps}^{-1} \) (83 ps), which remains constant regardless of the doping level. The competition between ET and carrier trapping can then be quantified by ET efficiency, \( \eta \), as plotted in Figure 4d.

\[
\eta = \frac{k_{ET}}{k_{ET} + k_{NR} + k_{Mn}} = \frac{k_{ET}}{k_{ET}} = \frac{k_{ET}}{k_1}
\]

The dependence of the \( \eta \) compiles with the PLQY depicted in Figure 1c. On the contrary, the Mn2+ emission efficiency after ET is independent of the doping levels, as evidenced by the constant emission lifetime, as shown in Figure 4b. Moreover, the lifetime of the slowest TA GSB components (i.e., \( \tau_2 \) in Figure 4d) decreases with the increasing Mn doping level. This component should be attributed to the other pool of QDs without dopant-Mn ET and the fast surface trapping. The shortened lifetime demonstrates the enhanced nonradiative recombination of excited charge carriers in this pool of QDs. Therefore, we can conclude that the evolution of the PLQY with the Mn doping should be dominated by (1) the competition between the dopant-Mn ET efficiency and the doping-induced trapping at Cl defect states and (2) the extra nonradiative recombination in the remaining QDs induced by the Mn doping.

Figure 5 summarizes the photoinduced charge-carrier dynamics in both undoped and doped QDs. There exist three different pools of undoped QDs (Figure 5a), where the photoexcited charge carriers in each pool will: (1) undergo fast surface trapping (3 ps) and then relax to the ground state nonradiatively (540 ps) (Pool A), (2) get trapped by PbCl states within 38 ps (Pool B), and (3) undergo intrinsic radiative recombination (15 ns) (Pool C). In doped QDs (Figure 5b), the situation in QD pool A remains insensitive to the doping level, whereas some extra fast nonradiative
recombination will occur in QD pool C to shorten the charge-carrier lifetime. In pool B of QDs, the dopant\textit{Mn} ET (28–79 ps) competes with the hole trapping (83 ps) at Cli states induced by Mn doping, which accounts for the change of the PLQY (Pool B). When the doping level is high (e.g., 38%), both the intrinsic emission in the host QDs and the Mn \textit{d--d} emission would be quenched, as proved by the faster emission decay in Figure 4b, resulting in the further declined PLQY, which is not discussed in Figure 5.

In conclusion, we have systematically studied the effect of Mn\textsuperscript{2+} doping on the photophysics of CsPbCl\textsubscript{3} QDs. Through DFT calculations, we demonstrated a change of main defect state from shallow PbCs electron traps to deep Cl interstitials (Cli) hole traps after Mn\textsuperscript{2+} doping. The investigation of the charge-carrier dynamics via time-resolved spectroscopies reveals the competition instead of mediation between the exciton--dopant ET and the hole trapping. Such competition rationalizes the nonmonotonic evolution of the PLQY with the doping level. Furthermore, because the ET to the Mn dopant mainly competes with the hole trapping, it is vital to passivate the hole traps to maximize the Mn\textsuperscript{2+} emission, for instance, by dual-doping\textsuperscript{26}.

Figure 4. (a) Rising edge of Mn emission kinetics from time-correlated single-photon counting (TCSPC) illustrating the ET. (The response function (RF) is set as a standard Gaussian pulse.) (b) TRPL kinetics of Mn-doped CsPbCl\textsubscript{3} with different concentrations measured in ms-TRPL with a milliseconds time window. (c) Rate constant of the components changes with the doping level following the same trend but displays higher values than the ET rates extracted from TRPL. (d) Calculated ET efficiency $\eta$ versus Mn concentration. $\tau_4$ is the time from TA fitting, which can be seen in Table S5.

Figure 5. Schematic diagram of the photophysical processes in (a) neat CsPbCl\textsubscript{3} QDs and (b) Mn-doped CsPbCl\textsubscript{3} QDs with appropriate Mn doping concentration.
preparation. Hence, this work provides a general model to optimize the structure of such nanomaterials.

**ASSOCIATED CONTENT**

* Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcl.0c01050.

Detailed methods for sample preparation, the characterization, DFT calculations, TEM images and size distribution, SEAD patterns, HADDF-STEM images of undoped and Mn-doped QDs, XPS spectra, DFT model and results, EPR analysis, rate constant equation model, TA spectra and fitting components, PLQY data, formation energy of the defect from DFT calculations, and TRPL kinetics (PDF)

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