Controlling Quantum Confinement and Magnetic Doping of Cesium Lead Halide Perovskite Nanocrystals

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ABSTRACT

Cesium lead halide (CsPbX$_3$) nanocrystals have emerged as a new family of semiconductor nanomaterials that can outperform existing semiconductor nanocrystals owing to their superb optical and charge transport properties. Although these materials are expected to have many superior properties, control of the quantum confinement and isoelectronic magnetic doping, which can greatly enhance their optical, electronic, and magnetic properties, has faced significant challenges. These obstacles have hindered full utilization of the benefits that can be obtained by using CsPbX$_3$ nanocrystals exhibiting strong quantum confinement or coupling between exciton and magnetic dopants, which have been extensively explored in many other semiconductor quantum dots. Here, we review progress made during the past several years in tackling the issues of introducing controllable quantum confinement and doping of Mn$^{2+}$ ions as the prototypical magnetic dopant in colloidal CsPbX$_3$ nanocrystals.

Key words : Lead halide perovskite, Quantum dot, Magnetic doping

1. Introduction

Semiconducting perovskite nanocrystals (NCs) have attracted much attention in recent years owing to their superb light-emitting properties and facile chemical tunability of the bandgap, making them particularly suitable for applications where they act as a photon$^{12,23}$ or charge carrier source.$^{3-6}$ Among various perovskite NCs, those in the cesium lead halide (CsPbX$_3$) system are among the most extensively explored prototypical perovskites owing to their relative ease of synthesis and potential for outperforming more commonly used II-VI or IV-VI semiconductor NCs in various applications. In particular, their ability to harvest photons to create charge carriers, transport them long distances,$^6$ and emit photons$^{18}$ are superior to those of many known semiconductor NCs. Fig. 1 shows the crystal structure of CsPbX$_3$, transmission electron microscopy (TEM) images of colloidal NCs of CsPbX$_3$, and a photograph showing the color-tunable fluorescence obtained by varying the halide composition.$^9$ Considering the successful application of various colloidal semiconductor NCs in recent decades in solar cells,$^{16-18}$ optoelectronics,$^{24-27}$ photonics, and biological applications,$^{18-20}$ one can easily see the potential of this new family of semiconductor NCs.

Here we will focus on colloidal NCs of CsPbX$_3$, with particular emphasis on controlling the quantum confinement and introducing a magnetic dopant into the host NC lattice. Without question, quantum confinement of the exciton is...
the most extensively explored phenomenon in various semiconductor NCs to obtain new properties unique to nanoscale semiconductor materials as distinct from their bulk counterparts. Furthermore, isoelectronic doping of paramagnetic ions into semiconductor NCs provides access to new optical, electronic, and magnetic properties not present in typical semiconductor NCs through exchange coupling between the exciton and dopant. However, introducing controlled quantum confinement and doping paramagnetic transition metal ions into CsPbX₃ NCs have been significantly more challenging than in many other semiconductor materials. Only very recently has meaningful progress been made to overcome the obstacles in performing these important tasks, enabling full exploration of the potential of this new type of semiconductor NC. Here, we review recent progress in the synthesis of colloidal quantum dots (QDs) of CsPbX₃ and Mn doping of various CsPbX₃ nanostructures.

2. Strongly Quantum-Confined CsPbX₃ NCs

In the typical hot injection synthesis condition, CsPbX₃ NCs with an edge length of > 10 nm are produced with a relatively broad size distribution. For CsPbBr₃, the exciton Bohr radius is 3.5 nm, so quantum confinement of the exciton is weak. For this reason, tuning of the bandgap in CsPbBr₃ NCs was achieved primarily by varying the halide (X) composition and changing the bulk band edge level rather than varying the quantum confinement of the exciton, in contrast to the procedure for QDs with a size-tuned bandgap. The post-synthesis anion exchange reaction was often used for this purpose.

Although it is still useful to vary the absorption and emission energy in CsPbX₃ via anion exchange, other material properties that result from confinement of the exciton require a controllable NC size. For instance, the exciton binding energy, the linewidth of fluorescence emission dictated by electron–phonon coupling, and the Rashba effect prominently observed in various lead halide perovskite NCs are expected to exhibit significant dependence on the quantum confinement. To explore such properties without encountering ensemble heterogeneity and utilize them in applications, the development of a robust method for the synthesis of size-controlled NCs in the quantum-confined regime is necessary. Although post-synthesis separation, often involving tedious multistage centrifugation of the heterogeneous NC sample, can improve the ensemble homogeneity, it is a rather inefficient approach to preparing uniform perovskite QDs for practical applications.

Much effort has been made recently to extend the size range of CsPbX₃ NCs into the strongly confined regime. However, the usual kinetic control (i.e., control of the growth via the reaction time) widely utilized for the synthesis of various other semiconductor NCs has not been very...
effective for size control of CsPbX$_3$ NCs owing to the rapid reaction conditions under typical hot injection synthesis.\(^9\) Furthermore, fast defocusing of the size after hot injection often resulted in a poor size distribution in ensembles of the NCs.\(^{39}\) One strategy that has been used to gain more control over the size of the NCs in the confined regime is to lower the reaction temperature. Generally, the NC size decreased with decreasing reaction temperature, giving access to more strongly confined QDs.\(^{40-42}\) However, the relatively large size distribution and contamination by NCs with other morphologies, such as nanoplatelets, remained an issue as reflected in the optical spectra exhibiting multiple excitonic peaks from different species (Fig. 2a). Another approach that has been taken to control the size is the use of different ligands (Fig. 2b–f).\(^{43}\) The exciton absorption peak from the nanoplatelets was often prominently superimposed on the absorption from the nanocubes, whereas the nanoplatelets leave a less distinct spectroscopic signature in the luminescence spectrum owing to their relatively low emission quantum yield compared to the bright nanocubes. Recently, Manna and coworkers reported that the size of CsPbBr$_3$ perovskite nanocubes can be reduced to ca. 4 nm by varying the composition or the amount of the ligands they used, specifically, the ratio of oleic acid to oleylamine (Fig. 3a).\(^{44}\) The size was reduced by suppressing the rapid ripening rate of the perovskite NCs during growth by reducing the quantity of ligands, which the authors considered to be responsible for ripening of the NCs. Because of the difference in the rate of ripening of perovskite NCs with different halides, size control via the ligand could not be extended to CsPbX$_3$ perovskite NCs with X = I. Recently, Pradhan and coworkers reported that the size of CsPbBr$_3$ NCs can be reduced by adding an oleylamine–HBr mixture to the reactant. The size of the NCs could be continuously tuned by varying the amount of the oleylamine–HBr mixture (Fig. 3b).\(^{45}\) They proposed that the size control mechanism is competition between Cs$^+$ and protonated ligands during growth of the NCs. All these methods rely on additional means to control the growth kinetics; therefore, the intrinsic heterogeneity of the size limits the spectroscopic homogeneity, which is crucial for various optical applications of this material.

Very recently, Son and coworkers developed a new synthesis approach that can produce strongly quantum-confined CsPbX$_3$ QDs with an unprecedented level of control over the size with ensemble uniformity.\(^{46}\) In contrast to the majority of other synthesis methods, which attempt to control the kinetic behavior of the reaction, the new approach developed by Son’s group used the thermodynamic equilibrium of halide ions to control the size. Fig. 3 compares the optical spectra and TEM images of CsPbBr$_3$ QDs synthesized by other methods exploiting control of the kinetics.

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**Fig. 3.** (a), (b), and (c) Absorption spectra and corresponding TEM images of QDs made in Refs. 44, 45, and 46, respectively. Images were modified with permission from Refs. 44, 45, and 46.
can be used. One crucial property of CsPbX₃ perovskite is a rare case in which the equilibrium approach solids for the majority of materials. However, lead halide a viable mechanism to control the size of nanocrystalline applicability of equilibrium-based synthesis. Although the differences in the chemistry and kinetics of reactions involving different halide elements in the earlier synthesis methods made it difficult to generalize the synthesis protocol to all halides, it is much easier to expand the thermodynamic equilibrium. (80–190°C), provides a condition in which the thermodynamic equilibrium. Moreover, this method is generally applicable to the synthesis of CsPbX₃ QDs of all three halides (Cl, Br, and I). Fig. 4a, b shows optical spectra and TEM images of QDs of CsPbCl₃ and CsPbI₃ prepared employing the same halide-equilibrium-based size control. Although the differences in the chemistry and kinetics of reactions involving different halide elements in the earlier synthesis methods made it difficult to generalize the synthesis protocol to all halides, it is much easier to expand the thermodynamic equilibrium. In general, thermodynamic equilibrium is not considered a viable mechanism to control the size of nanocrystalline solids for the majority of materials. However, lead halide perovskite is a rare case in which the equilibrium approach can be used. One crucial property of CsPbX₃ NCs and related lead halide perovskite materials that allows the use of thermodynamic equilibrium for size control is the highly labile halide ions in the crystals. It is well known that a lead halide perovskite NC can undergo facile anion exchange even at room temperature owing to its low kinetic barrier to diffusion in the lattice. The low kinetic barrier, especially at the elevated temperatures used in hot injection (80–190°C), provides a condition in which the thermodynamic equilibrium of the halide becomes a more relevant control. The other crucial property of CsPbX₃ NCs is the size-dependent composition of the halide resulting from the halide-rich surface of the NCs. The relative halide content increases with decreasing QD size. This allows the equilibrium of halide ions at the interface of the NCs and the solvent medium to determine the size of the NCs. Size control was achieved either by varying the amount of halide in the reactant mixture for a given amount of Cs and Pb at a fixed reaction temperature or by varying the temperature for a fixed amount of the precursors of all three elements constituting the perovskite QDs, as shown in Fig. 4c, d, respectively. Through the law of mass action, smaller QDs were obtained when the concentration of halides increased for a fixed reaction temperature and concentrations of Cs and Pb.

Because size control is achieved via thermodynamic equilibrium, the size of the QDs was independent of the nucleation and growth kinetics, which is one of the most distinctive and advantageous features of equilibrium-based synthesis. Fig. 5a, b shows the identical absorption and emission spectra of CsPbBr₃ QDs synthesized with various reaction quenching times and precursor injection rates, which prove that size control occurs via thermodynamic equilibrium and not kinetic control. The mechanism of size control through halide equilibrium between the QD lattice and solvent medium is illustrated by the simple model shown in Fig. 5c. In this model, control of the QD size (l) by varying the Br concentration ([Br⁻]) can be viewed as satisfying the following equilibrium condition.

$$\mu_{\text{Br}^-_{\text{sol}}}([\text{Br}^-], T) = \mu_{\text{Br}^-_{\text{QD}}}(l, T)$$  \hspace{1cm} (1)

$$\mu_{\text{Br}^-_{\text{sol}}}([\text{Br}^-], T)$$ is the chemical potential of Br⁻ at a given [Br⁻] value and temperature T in the solution medium. $$\mu_{\text{Br}^-_{\text{QD}}}(l, T)$$ is the chemical potential of Br⁻ in the lattice of QDs with size l at temperature T, which depends on the relative stoichiometric composition of Br⁻. $$\mu_{\text{Br}^-_{\text{sol}}}([\text{Br}^-], T)$$ should increase approximately logarithmically with [Br⁻] following $$\mu_{\text{Br}^-_{\text{sol}}}([\text{Br}^-], T) = \mu_{\text{Br}^-_{\text{sol}}}^{o} + RT \ln([\text{Br}^-])$$, where

![Fig. 4. Absorption and PL spectra and TEM images of (a) CsPbCl₃ and (b) CsPbI₃ QDs obtained via halide equilibrium control method, with the corresponding TEM images. The spectra show clear excitonic features, and the TEM images show size and shape uniformity. (c) Change in size of CsPbBr₃ QDs with constant temperature and various Br/Pb ratios. (d) Change in size of CsPbBr₃ QDs with various temperatures and constant Br/Pb ratio. Images were modified with permission from Ref. 46.](image-url)
μ_{Br^{-},sol}, R, and γ are the chemical potential in the standard state, gas constant, and activity coefficient, respectively. The larger slope of μ_{Br^{-},sol}([Br'−], T) at lower ([Br']−) and the decreasing size dependence of μ_{Br^{-},QD}(l, T) for larger QDs explains the less uniform size of the previously reported larger NCs synthesized by typical hot injection synthesis using a lower [Br'−] value, i.e., a Br/Pb ratio of 2.

3. Mn Doping of CsPbX3 NCs

Isolelectronic doping of semiconductor NCs with paramagnetic transition metal ions has been extensively investigated as a way to introduce new optical, electronic, and magnetic properties through the interaction between the exciton and d electrons of the dopant ions. For instance, II-VI QDs, such as MX (where M = Cd, Zn and X = S, Se) doped with Mn^{2+} can generate intense sensitized dopant luminescence, creating a magnetically coupled exciton state enabling optical control of the magnetism, or produce energetic hot electrons via exciton-to-hot-carrier upconversion.\(^{26,48}\) Although it is not the focus of this article, it is worth mentioning that doping of lanthanide rare-earth metal ions has also been extensively investigated, where quantum cutting of high energy photons into low energy photons has been a topic of particular interest.\(^{49}\)

Because CsPbX₃ NCs were introduced as a new semiconductor NC material that can outperform many existing ones, doping of Mn²⁺ into these materials has been extensively attempted in recent years in anticipation of the benefits seen in other semiconductor hosts. The first successful Mn doping of CsPbX₃ NCs was reported in CsPbCl₃, where hot injection synthesis of CsPbCl₃ NCs in the presence of an additional Mn precursor resulted in low-level doping of Mn from less than 1% up to 10%.\(^{27,29}\) In this synthesis, MnCl₂ was the most effective precursor of Mn ions, whereas many other organometallic precursors such as Mn(acac)₂, Mn(acac)₃, and Mn(oleate) were very ineffective as dopant precursors. When MnCl₂ was used as the Mn precursor and CsPbBr₃ was used as the host material, the resulting NCs were Cl/Br mixed-halide NCs doped with Mn. However, MnBr₂ could not be used as a viable precursor of Mn ions for either CsPbCl₃ or CsPbBr₃ as the host under the hot injection synthesis condition, as will be discussed further later. Fig. 6a shows the absorption spectra of the undoped and Mn-doped CsPbCl₃ and CsPb(Cl/Br)₃ NCs synthesized using MnCl₂ as the Mn precursor at a doping concentration of less than 1%. Fig. 6b shows the corresponding luminescence spectra. In the Mn-doped NCs, characteristic Mn luminescence near 600 nm appeared, indicating successful doping of Mn into perovskite NC hosts with a sufficiently large bandgap, which can exhibit exciton–Mn energy transfer. The time-resolved Mn luminescence data shown in Fig. 6c can be fitted to a single exponential, indicating a relatively

Fig. 5. (a) Absorption and PL spectra of CsPbBr₃ NCs quenched for 5 s (blue line) and 50 s (orange dashed line), (b) absorption and PL spectra of CsPbBr₃ NCs with cesium oleate injected swiftly (blue line) and over 4 s dropwise (orange dashed line), (c) Proposed mechanism of halide equilibrium control of quantum confinement in Cs-based lead halide QD synthesis. Images were modified with permission from Ref. 46.

Fig. 6. (a) Absorption and (b) PL spectra of Mn-doped CsPbCl₃ and CsPbClₓBr₃₋ₓ nanocrystals with those of undoped control samples. (c) Time-dependent PL decay of Mn phosphorescence. Images were modified with permission from Ref. 27.
homogeneous ligand field environment of the dopant ions, which is consistent with a low doping level. One of the issues in characterizing the detailed structure of Mn-doped perovskite NCs is quantifying the doping concentration, which can easily be overestimated owing to difficulties in removing the remaining Mn ions. Unlike many other semiconductor NCs, perovskite NCs are unstable in polar solvents, severely limiting the range of usable solvents for removing unreacted metal salts via the solvent/antisolvent approach. To overcome this issue, Son and coworkers utilized gel permeation chromatography (GPC), a technique optimized by Greytak and coworkers for cleaning II-VI QDs, to remove the excess unreacted Mn and obtain a more reliable doping concentration in the thoroughly cleaned samples. Fig. 7 shows the evolution of the absorption and emission spectra as well as the measured doping concentration after each cycle of GPC purification of the NCs. After more than four GPC cycles, the measured Mn doping concentration reached a plateau, while the same absorption and emission intensity were maintained. This demonstrates clearly the necessity for thorough removal of remaining Mn ions in the solvent for accurate quantification of the doping.

![Fig. 7](image-url)

**Fig. 7.** (a) Absorption and (b) PL spectra of washed CsPbCl$_3$:Br$_{3-x}$ sample. (c) Tested Mn doping concentration of samples with different numbers of washings. Images were modified with permission from Ref. 27.

![Fig. 8](image-url)

**Fig. 8.** (a) Absorption and PL spectra of CsPbCl$_3$ sample with high Mn doping concentration (~ 46%). (b) TEM images of CsPbCl$_3$ NCs with high Mn doping concentration. Inset shows photograph of Mn-doped CsPbCl$_3$ NCs under UV excitation. Images were modified with permission from Ref. 51. (c) Method to dope Mn in CsPbCl$_3$ NCs using an ammonium chloride mixture. (d) PL spectra of CsPbCl$_3$ NCs acquired with increasing amount of ammonium chloride mixture. Images were modified with permission from Ref. 52.
concentration.

In later works on Mn-doped CsPbCl$_3$ NCs, the hot injection synthesis protocol was further optimized to increase the doping concentration. Yang and coworkers were able to reach a doping concentration of 46% and luminescence quantum yield of 56% by using a large amount of excess Mn precursors (e.g., a Pb/Mn ratio of 1:10). Fig. 8a, b shows the absorption and emission spectra and TEM images of the highly Mn-doped CsPbCl$_3$ NCs. Pradhan and coworkers took another approach to increasing the efficiency of Mn doping, where they used oleylamine chloride as an additional reactant that can boost the doping efficiency. They observed a large increase in the Mn luminescence intensity with increasing amount of oleylamine chloride for a given amount of Mn precursor (Fig. 8c, d). The authors attributed the increased efficiency of Mn doping to the formation of a higher concentration of NCs during the early phase of the reaction, which increased the probability of Mn doping, although the validity of this explanation is not yet fully established.

More recent synthesis of Mn-doped CsPbCl$_3$ has expanded the reaction conditions beyond the hot injection condition. Meijerink and coworkers showed examples of room-temperature synthesis methods for Mn doping of CsPbCl$_3$ with non-halide Mn precursors. In their first report, they used metal acetate salts as the precursor, which were converted to metal oleate complexes in the presence of ligands, and then added HCl to protonate the carboxylate group, increasing the amount of monomer initiating the formation of nanocubes. HCl also created a Cl-rich surface, supplying ample binding sites for Mn$^{2+}$ ions and facilitating Mn doping. Further coating of Mn-doped CsPbCl$_3$ with an additional CsPbCl$_3$ shell improved the Mn luminescence quantum yield.

Although earlier efforts to synthesize Mn-doped CsPbCl$_3$ NCs produced relatively large cube-shaped NCs that experience very weak quantum confinement, several recent studies reported the synthesis of CsPbCl$_3$ nanoplatelets with strong confinement in one dimension. Nag and coworkers synthesized Mn-doped CsPbCl$_3$ nanoplatelets with a thickness of 2.2 nm, which imposes strong confinement along the thickness direction, by a room-temperature reaction. They were also able to vary the doping concentration in the range of 0.2–2%. Pradhan and coworkers reported another method of generating Mn-doped CsPbCl$_3$ nanoplatelets, which involves the initial synthesis of a Mn-doped monolayer structure and subsequent formation of nanoplatelets by the addition of Cs-oleate. They produced 5-nm-thick nanoplatelets with a relatively large lateral dimension in the range of 20–580 nm, which varied with the concentration of Cs and Mn during the reaction. Because quantum confinement of the exciton in Mn-doped semiconductor NCs can enhance the exciton–dopant interaction, which determines various magnetooptical properties, continued progress in the synthesis of strongly confined Mn-doped perovskite NCs will be important for expanding their applicability.

Most of the work on Mn doping of CsPbX$_3$ NCs has focused on CsPbCl$_3$ despite its less favorable optical properties, such as a higher bandgap and lower luminescence quantum yield, which are presumably due to its higher defect density compared to other halide perovskites. This is because doping of Mn is most favorable in CsPbCl$_3$ and becomes increasingly difficult for bromide and iodide perovskite hosts. To date, successful doping of Mn in a CsPbBr$_3$ NC host could not be achieved by simply extending the doping method used for producing Mn-doped CsPbCl$_3$ NCs. Klimov and coworkers hypothesized that direct hot injection synthesis of Mn-doped CsPbBr$_3$ using MnBr$_2$ was energetically unfavorable owing to the large difference in bond energy between Pb–Br (249 kJ/mol) and Mn–Br (314 kJ/mol) compared to that between Pb–Cl (301 kJ/mol) and Mn–Cl (338 kJ/mol). They argued that the higher stability of the Mn–Br bond compared to the Pb–Br bond impeded the incorporation of Mn into the CsPbBr$_3$ lattice. Although it is still not clearly understood yet, the difference in the thermochemistry can certainly be a factor affecting the ability to dope Mn into different CsPbX$_3$ NCs.

There are several reports of attempts to utilize the ion exchange reaction to obtain Mn-doped CsPbBr$_3$ NCs. For instance, anion exchange of Mn-doped CsPbCl$_3$ with Br$^-$ resulted in not only the exchange of anions but also removal of doped Mn ions in the host lattice. Others attempted cation exchange of Pb with Mn in CsPbBr$_3$ using MnCl$_4$. However, this also resulted in anion exchange, ultimately forming Mn-doped NCs with Cl$^-$ as the dominant anion in the lattice. Chen and coworkers claimed that they were able to dope Mn into CsPbBr$_3$ and that it increased the stability of the NCs significantly, although they did not observe Mn emission from their sample. Xu and Meijerink recently argued that the absence of Mn emission in Mn-doped CsPbBr$_3$ is not due to a lack of dopant ions in the lattice but due to back-energy transfer from Mn to the host, which effectively quenches the Mn luminescence. Similar to the case of Mn-doped II-VI QDs, where the bandgap of the host is not sufficiently large compared to the Mn ligand field transition energy to allow effective unidirectional energy transfer from the exciton to Mn.

Recently, Son and coworkers developed a more robust synthesis method that produces Mn-doped CsPbBr$_3$ NCs that exhibit intense Mn luminescence. The synthesis was a two-step procedure in which they first synthesized a Mn-doped monolayer structure ($L_x$[Pb$_{1-x}$Mn$_x$Br$_4$]) by adding Cs-oleate (Fig. 9a). In this method, HBr was used to facilitate the formation of a stable $L_x$[Pb$_{1-x}$Mn$_x$Br$_4$] monolayer structure. Mn doping of this monolayer structure was clear from the observation of intense Mn luminescence upon excitation of the host structure at 370 nm. The absorption and emission spectra of $L_x$[Pb$_{1-x}$Mn$_x$Br$_4$] are shown in Fig. 9b, c, respectively. The absorption spectrum, which has a sharp absorption peak at 395 nm, is very similar to that of a $L_x$[PbBr$_4$] monolayer.
reported previously, indicating that the $L_2[Pb_xMn_{1-x}Br_4]$ is essentially a Mn-doped monolayer structure of $L_2[PbBr_4]$. On the other hand, the luminescence is centered at 620 nm and arises entirely from Mn. The similarity of the absorption and photoluminescence excitation (PLE) spectra of $L_2[Pb_xMn_{1-x}Br_4]$ proved that the Mn luminescence in this monolayer structure is also sensitized. The intensity of the Mn luminescence in the $L_2[Pb_xMn_{1-x}Br_4]$ monolayer structure was well correlated with the amount of HBr used, which indicated that HBr facilitates doping of Mn into this structure. $L_2[Pb_xMn_{1-x}Br_4]$ often forms a multilayer structure when dried, as indicated by a series of small-angle diffraction peaks separated by $2\theta = 2.2^\circ$ in the powder X-ray diffraction patterns, which corresponds to a 4.1 nm spacing between the stacked layers separated by the ligand. When Cs-oleate was added to the solution of the $L_2[Pb_xMn_{1-x}Br_4]$ monolayer structure at 200°C, Mn-doped CsPbBr$_3$ NCs were formed. Interestingly, the resulting product was a mixture of Mn-doped CsPbBr$_3$ NCs with two different morphologies, i.e., nanocubes (6.5–8.5 nm) and nanoplatelets (~2 nm in thickness). However, the two species could be readily separated via centrifugation, providing access to NCs of two different dimensions. The Mn luminescence intensity of the Mn-doped CsPbBr$_3$ nanocubes was well correlated with that of the $L_2[Pb_xMn_{1-x}Br_4]$ monolayer structure, showing an increase with the amount of HBr used during the initial formation of the $L_2[Pb_xMn_{1-x}Br_4]$ monolayer structure (Fig. 9d–f). This suggests that the formation of $L_2[Pb_xMn_{1-x}Br_4]$, which contains the same Mn–Br coordination present in Mn-doped CsPbBr$_3$ NCs, is crucial to formation of Mn-doped CsPbBr$_3$ NCs under a hot injection condition. The robustness of the Mn–Br bond in $L_2[Pb_xMn_{1-x}Br_4]$ was demonstrated by the strong Mn luminescence, which survived even at 120°C. It is also notable that unlike the Mn-doped CsPbBr$_3$ nanocubes, which exhibited both exciton and Mn luminescence, the Mn-doped CsPbBr$_3$ nanoplatelets exhibited primarily Mn luminescence, as can be determined easily from the color of
the luminescence (Fig. 9a). This may reflect the potentially more rapid exciton–Mn energy transfer rate in the partially quantum confined nanoplatelets compared to that in the only weakly quantum confined nanocubes.

Because doping of Mn$^{2+}$ ions into semiconductor NCs creates new optical, electronic, and magnetic properties resulting from exchange coupling between the exciton and dopant, the magnitude of the coupling is an important subject of investigation. It was explored quite extensively in II-VI Mn-doped semiconductor NCs as a function of the structural parameters, which affect the spatial overlap of the exciton and dopant wavefunction dictating the strength of the exchange coupling of the exciton and dopant.\cite{60,61}

For the Mn-doped CsPbX$_3$ NC system, Son and coworkers performed the first experiment to provide useful information on the strength of the exciton–dopant exchange coupling in comparison to that in Mn-doped II-VI semiconductor NCs.\cite{62}

The approach taken was to compare the exciton–Mn energy transfer times ($\tau_{ET}$) of Mn-doped CsPbCl$_3$ NCs and Mn-doped CdS/ZnS NCs after normalizing to the doping concentration. In their study, $\tau_{ET}$ was obtained by comparative analysis of the exciton relaxation dynamics in Mn-doped and undoped NCs using pump–probe transient absorption spectroscopy to monitor the dynamics of exciton relaxation.

The energy transfer pathway that exists only in Mn-doped NCs was manifested as an additional dynamic component in the bleach recovery of the exciton, as shown in Fig. 10a. In Mn-doped CsPbCl$_3$ nanocubes with an edge length of 10 nm and a ~ 0.4% doping concentration, $\tau_{ET}$ was determined to be ~ 380 ps.\cite{62} Compared to the $\tau_{ET}$ value of the previously studied Mn-doped CdS/ZnS NCs after correcting for the difference in doping concentration, the $\tau_{ET}$ in the Mn-doped CsPbCl$_3$ nanocubes is 2–5 times slower. The authors concluded that although this may suggest that the exciton–Mn exchange interaction is weaker than that in the II-VI semiconductor NC host, the significant difference in the quantum confinement in the two NC samples should also be considered to make a more meaningful comparison. Because the exciton in Mn-doped CsPbCl$_3$ nanocubes with an edge length of 10 nm is very weakly confined, in contrast to that in the much smaller Mn-doped CdS/ZnS NCs, the comparison of $\tau_{ET}$ in their study may underestimate the relative strength of exciton–Mn coupling in Mn-doped CsPbCl$_3$ nanocubes. Clearly, further investigation of other Mn-doped CsPbX$_3$ NCs with different halide compositions and varying degrees of quantum confinement is necessary to obtain a better picture of the coupling between the exciton and dopant in this system.

### 4. Outlook and Conclusion

Although the first chemical synthesis of colloidal CsPbX$_3$ perovskite NCs was reported only several years ago, much progress has been made since then in both the synthesis and characterization of CsPbX$_3$ NCs with much higher control of the dimensions and chemical composition. One of the most important achievements in the synthesis of CsPbX$_3$ perovskite NCs was the development of methods to precisely control the quantum confinement with very high ensemble uniformity of the morphology and size in the strongly confined regime. This opened the door to exploitation of quantum confinement of excitons in perovskite NCs for their application, which had been lagging compared to that of other semiconductor NCs. Another notable achievement in the synthesis of colloidal CsPbX$_3$ perovskite NCs was successful doping with paramagnetic transition metal ions such as Mn$^{2+}$. This provided access to various new optical, electronic, and magnetic properties originating from the coupling of the exciton and magnetic dopant ions that are not present in undoped perovskite NCs. Although the ability to control the quantum confinement and introduce magnetic dopants into the lattice of CsPbX$_3$ NCs was acquired only recently, methodologies have rapidly expanded to CsPbX$_3$ NCs of different dimensions beyond simple nanocubes. With continuing development of the synthesis of CsPbX$_3$ NCs with higher levels of structural and chemical control, it will also be necessary to explore the structure–property relationship and use the new properties in applications.

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