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Chemically Tailoring the Dopant Emission in Mn doped $CsPbCl_3$ Perovskite Nanocrystals

Samrat Das Adhikari, Sumit K. Dutta, Anirban Dutta, Amit K. Guria and Narayan Pradhan*

Abstract: Doping in perovskite nanocrystals adopts different mechanistic approach in comparison to widely established doping in chalcogenide quantum dots. The fast formation of perovskites makes the dopnat insertions more competitive and challenging. Introducing alkylamine hydrochloride (RNH_3Cl) as a promoting reagent, precise controlled doping of Mn(II) in $CsPbCl_3$ perovskite nanocrystals is reported. Simply, by changing the amount of RNH_3Cl, the Mn incorporation and subsequent tuning in the excitonic as well as Mn d-d emission intensities are tailored. Investigations suggested that RNH_3Cl acted as the chlorinating source, controlled the size, and also helps in increasing the number of particles. This provided more opportunity for Mn ions to take part in reaction and occupied the appropriate lattice positions. Carrying out several reactions with varying reaction parameters, the doping conditions are optimized and the role of the promoting reagent for both doped and undoped systems are compared.

Doping in perovskite nanocrystals opens up a new era of current research.[1] Beyond the widely established color tunable bandedge emissions of halide perovskites,[2] on doping with appropriate dopants the optical emission of these nanocrystals might further tune to a new spectral window.[1h,3] For covalent chalcogenide nanocrystals where the classical mechanism of crystal growth is largely understood, doping is established as a phenomenon of surface adsorption.[4] Here, dopants ions are adsorbed onto the energetically favorable facets of the host nanocrystals during growth. However, in inorganic halide perovskite nanocrystals the fundamentals of crystal growth is still not widely understood and typically being ionic crystals, reaction proceeds much faster. Hence, the adsorption mechanism which needs controlled nanocrystals growth became difficult for perovskites doping. Another doping process adopted for chalcogenides is via ion diffusion where dopant ions are selectively exchanged or diffused inside the host crystal.[4e,5] However, achieving control over precise ion exchange in dopant level is yet to be established in perovskite nanocrystals.[4f] Hence, doping in these nanocrystals remains challenging and needs deeper fundamental understanding of the crystal formation and also developments of facile synthesis procedures.

Among various transition metal dopants, doping Mn(II) ion in chalcogenides nanocrystal hosts is largely understood.[4a,5g,6] The uniqueness of this dopant is its long lifetime spin polarized d-d emission in yellow-orange spectral window. For perovskite hosts, the compatible band alignment and efficient host exciton energy transfer to Mn states are more favorable in $CsPbCl_3$.[1h] As Mn (II) ions reside on Pb(II) positions in the crystal lattice, a competitive reactiveness of the Mn precursor along with Pb is highly required for efficient Mn insertions.[1h] At the desired reaction temperature (180-200 °C), being the reaction is very fast, introduction of sufficient Mn(II) precursor concentration is required for establishing a favorable condition for inserting only a few percentage of Mn in the host crystal.[1h] Hence, this demands more facile approach and in-depth study of the reaction chemistry for exploration of doping in perovskite nanocrystals.

Understanding the chemical pathways of formation of $CsPbCl_3$, herein, the doping of Mn ions is successfully achieved with minimal Mn(II) precursor by introducing a reaction activating agent alkylamine hydrochloride (RNH_3Cl). The intensity of the dopant emission is tailored with the function of the amount of added RNH_3Cl. Importantly; the approach did not require the traditional follow up fast cooling process, rather constantly maintained at 180-200°C. Investigation suggested that RNH_3Cl helped in creating more number of particles with smaller dimension which provided more opportunity for Mn(II) to take part in a comparatively slow process. Contrary to similar previous reports, here successful doping was achieved with initial 5% Mn precursor (with respect to Pb) in the reaction, which effectively doped ~1.3 % Mn; a breakthrough of doping in ionic solids. The emission was also observed bright (QY ~27 %) with minimal host excitonic emission. The effect of RNH_3Cl on synthesis of both doped and undoped systems are investigated in relation to size tuning, percentage of dopant ions incorporation and the tailoring of the optical emissions and are reported in this communication.

For doping Mn(II) in $CsPbCl_3$ nanocrystals, high temperature synthetic protocol, typically between 180-200 °C, was adopted. Molten RNH_3Cl (mixture of oleylamine and HCl, see experimental section in Supporting Information) was introduced in the reaction flask along with $PbCl_2$, $MnCl_2$ and other reagents. At ~180 °C, Cs-precursor was swiftly injected. Samples were collected as a function of time and also the amount of RNH_3Cl, and analyzed. Figure 1a shows the schematic presentation of the reaction and the formation of Mn doped $CsPbCl_3$ (Mn:$CsPbCl_3$) nanocrystals. The reagent RNH_3Cl, may be obtained from HCl and several alkylamines (octyl, dodecyl, hexadecyl etc.) though for liquid nature at room temperature oleylamine was preferred. Under illumination, the digital image of the reaction flask containing Mn:$CsPbCl_3$ nanocrystals is shown in Figure 1bwhere the orange color preliminarily reflected as their origin from Mn d-d emission. The absorption and photoluminescence (PL) spectra of undoped $CsPbCl_3$ obtained in similar reaction in presence of 0.5 ml RNH_3Cl are shown in Figure 1c.PL spectra of Mn:$CsPbCl_3$ nanocrystals normalized at the exciton emission are shown in Figure 1d. For understanding the impact of concentration of RNH_3Cl, the distinctive PL spectra of Mn:$CsPbCl_3$ nanocrystals obtained with variable amount of RNH_3Clat normalized OD (370 nm) are presented in Figure 1e-h. As observed, the intensity of the excitonic blue emission slowly diminished with evolution of intense Mn d-d emission at 585 nm. Mn and Pb precursor, and

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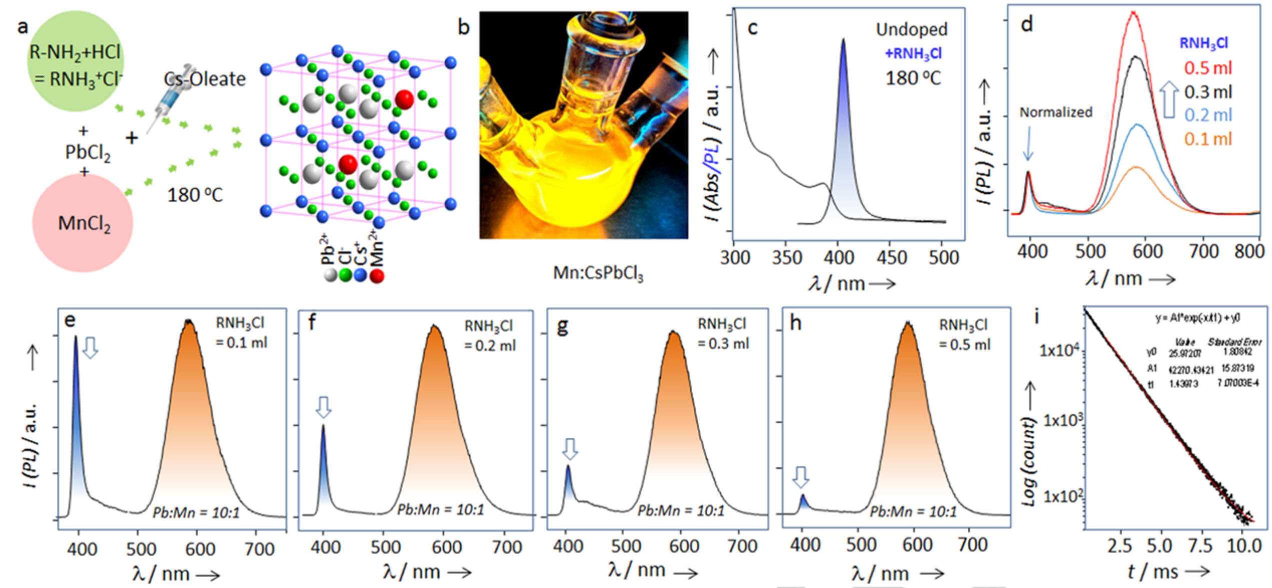

Figure 1.(a) Schematic presentation of the synthesis of Mn doped $CsPbCl_3$ nanocrystals using RNH_3Cl as the activating reagent. Atomic model shows the placement of Mn(II) in substitution position of Pb(II) in $CsPbCl_3$ crystal lattice. (b) Digital image showing Mn doped $CsPbCl_3$ nanocrystals in reaction flask under illumination. (c) Typical UV-vis and PL spectra of $CsPbCl_3$ nanocrystals obtained without Mn precursor. (d) Overlapped PL spectra obtained in similar reactions with variable RNH_3Cl concentration normalized at the excitonic emission. (e-h) PL spectra showing dual emissions with successive increase of amount of RNH_3Cl in the reaction mixture. $MnCl_2$ was taken 5 mole percentages to $PbCl_2$. For all these spectra, samples were taking after 1 min of injection of Cs precursor at 180 °C without following the ice cooling approach. (i) Excited state decay lifetime of Mn d-d emission (Emission at 585 nm). Excitation wavelength is 370 nm.

also all other reactants were unchanged in all these reactions. Photoluminescence excitation (PLE) spectra presented in Figure S1 showed the bandedge for all cases remained overlapping reflecting the Mn emission originated from the host $CsPbCl_3$ nanocrystals. The excited state decay lifetime suggested the long lifetime of ~1.4 ms (Figure 1i) which was typical for Mn d-d emission. All these results suggest Mn(II) ions are doped in $CsPbCl_3$ perovskite nanocrystals.

Before investigating the correlation of the amount of RNH_3Cl salt taken in the reaction system with the percentage of Mn incorporation, control reactions without the salt were performed. Reactions with fast cooling and also retaining at 180 °C were compared. Figure 2 presents the PL spectra of series of reactions with varying the Mn concentration (with respect to Pb) from 2 to 100% both in presence (Figure 2a) and absence (Figure 2b) of RNH_3Cl. Interestingly, it was observed that the intense Mn-emission with minimal exciton emission was observed even with 5 % of Mn(II) precursor in presence of RNH_3Cl. However, under identical reaction conditions, with increase of Mn concentration further did not improve the PL intensity suggesting 5 % Mn might be enough for obtaining the optimized Mn doped $CsPbCl_3$ nanocrystals in our reaction conditions. In contrast, without salt no Mn d-d emission appeared with this amount of Mn(II) precursor. It has been noted that even with 5 % Mn taken along with RNH_3Cl, the relative intensity of the Mn-emission with respect to exciton emission was superior to that of 100 % $MnCl_2$ taken without the salt. These observations clearly concluded that the RNH_3Cl helped significantly on the doping of Mn in $CsPbCl_3$ nanocrystals.

Presence of Mn in all the above samples were measured by energy dispersive spectral (EDS) analysis and only ~1-8 % Mn (with respect to Pb) of was observed in these samples. For

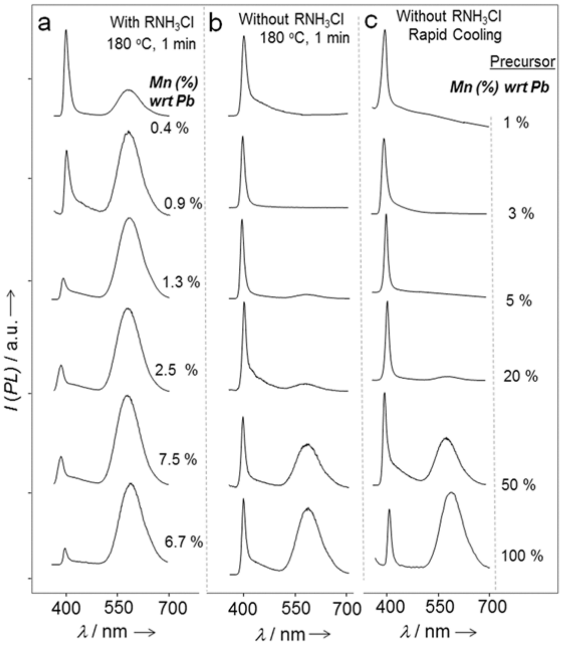

Figure 2. PL spectra of Mn doped $CsPbCl_3$ nanocrystals obtained (a) in presence of 0.5 ml RNH_3Cl, (b) in absence of RNH_3Cl keeping the reaction at 180 °C and (c) without $RNH_3Cl$with rapid cooling to room temperature after Cs precursor injection. Right hand panel shows the molar percentage of Mn with respect to Pb. Amount of Mn with respect to Pb ions is shown in inset of (a) and (c). Representative absorption spectra for these PL spectra are shown in Figure S2.

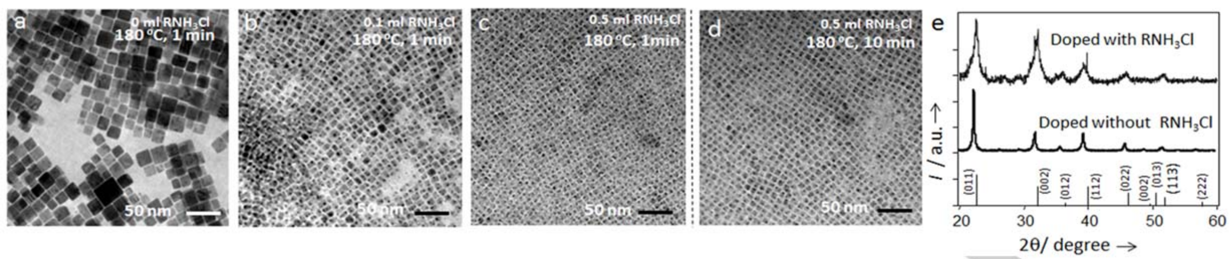

Figure 3. (a-c) TEM images of doped $CsPbCl_3$ nanocubes obtained from samples without and with 0.1 ml and 0.5 ml RNH_3Cl taken in the reaction flask. (d) TEM image of doped $CsPbCl_3$ nanocubes obtained with 10 min annealing at 180 °C with 0.5 ml RNH_3Cl. (e) Powder XRD patterns from the doped nanocrystals with and without RNH_3Cl and both samples collected after 1 min annealing at 180 °C. More TEM images are provided in Figure S4.

50% Mn precursors with respect to Pb, led to only 7.5 % Mn in the purified sample (Figure S3); but the best emission with 5% Mn could replace only 1.3 % Pb to Mn in the crystal lattice (inset, Figure 2). Point EDS on transmission electron microscope (TEM) was chosen as the appropriate tool as it was associated with small area.

While above spectra were obtained from the samples collected at 180°C from the reaction, samples collected from room temperature after rapid cooling following traditional approach were also measured for comparison. Figure 2c shows the PL spectra obtained with varying $MnCl_2$ concentration and ice cooling the flask after Cs-oleate injection without the activating chloride reagent, RNH_3Cl. Unfortunately, no significant difference in the evolution of Mn d-d emission was observed even with 5 % or more $MnCl_2$ concentration. This clearly suggested that RNH_3Cl became the promoting reagent which helped efficient doping at elevated reaction temperature and with minimum Mn precursor concentration.

Correlating further the concentration dependency of RNH_3Cl for tailoring the Mn d-d emission, microscopic images of all samples in presence and absence of RNH_3Cl were analyzed. Very interestingly, it was observed that for nanocrystals obtained without RNH_3Cl showed nanocubes having average diameter ~25 nm (Figure 3a), but a drastic reduction of size was noticed in presence of RNH_3Cl (Figure 3b,c and Figure S5). Further, it was observed that with variation of the amount of RNH_3Cl, the average size of nanocubes varied. For 0.1 ml and 0.5 ml RNH_3Cl, approximately nanocubes having average edge length ~ 12 and ~ 8 nm were obtained. Histograms showing the size distribution for these three sets of images are shown in Figure S6. While, all these cases the reaction temperature was fixed at 180 °C, the size for the traditional reaction following ice cooling approach under similar condition was also measured. Interestingly, it was observed that the cube size maintained ~ 12 nm (Figure S7). Further, for understanding the role of Mn, all the reactions were carried out without Mn which had similar trend suggesting the amount of $MnCl_2$ used here had no impact either on the shape or the size. However, the contrasting observation was noticed with prolonged annealing of the nanocrystals. In absence of RNH_3Cl these were turned to bulk (Figure S8), but interestingly, in presence of RNH_3Cl the size remain unchanged. Figure 3d shows the TEM image of sample obtained after 10 min of annealing from the reaction with 0.5 ml RNH_3Cl and the size was ~ 8 nm and this was same as in Figure 3c. The dark spot on the TEM images of these nanocubes are the Pb(0) which were formed under electron beam and not in solution. Powder X-ray diffraction (XRD) patterns for these samples are shown in Figure 3e and the obtained peak position resembled with cubic phase of $CsPbCl_3$ (JCPDF: 84-0438). The FWHM of the peaks suggested that the larger size particles for the nanocrystals obtained in absence of RNH_3Cl and this resembled with obtained TEM images. These results further concluded that the fast cooling might not be required for obtaining either doped or undoped $CsPbCl_3$ nanocrystals.

All the above results obtained in presence of RNH_3Cl corroborated that the chlorinating agent could control the size and also stabilize the nanocrystals at higher temperature. It could be further stated that number of nanocubes increased with decrease of their size as a function of increase in the amount of RNH_3Cl. This is assumed considering Cs precursor is the limiting reagent and reacts completely during the nanocrystals formation. Hence, RNH_3Cl only controlled the density of formation of particles. As more particles were formed, this provided more opportunity for Mn(II) precursor to react along with Pb(II). This allowed more particles got Mn doped. However, it was indeed difficult to calculate the amount of Mn atoms present per particle, rather its percentage as a whole was assumed in all of our experiments. The function of RNH_3Cl was expected simply providing controlled amount of chloride as per the demand of the reaction. More chlorinating agent means more amount of supply of chloride ions and this helped reaching the critical concentration for nucleation faster.

Apart from typical cube shape, the doping was also performed in platelet shaped $CsPbCl_3$ nanostructures. While all the above experiments were carried out with Cs to Pb precursor ratio 1:5 and with 0.5 ml RNH_3Cl; but interestingly, with 1:2 ratio the shape turned to mostly 2D platelets. The TEM images and XRD pattern obtained from the nanostructures are presented in

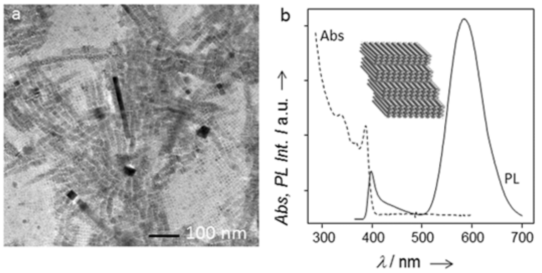

Figure 4. (a) TEM image of stacked $CsPbCl_3$ platelets. (b) Absorption and PL spectra of Mn doped $CsPbCl_3$ platelets. Inset shows the schematics of platelet stacking. More TEM images are provided in Figure S8.

Figure 4a (also Figure S9) and Figure S10 respectively. Platelets were observed stacked or self-assembled in the images and these were also in cubic phase. The UV-visible and PL spectra of these nanostructures are shown in Figure 4b which shows intense Mn d-d emission, and the dual emission ratio remained almost same like our best doped nanocubes with 5% Mn and 0.5 ml RNH_3Cl.

The quantum yield (QY) of our best sample was 27 % standardized following the procedure mentioned in our previous report.[6b] We focused here the relative intensity ratios of the dual emissions as the function of concentration of the additive salt and hence different literature reported QYs were not compared.

In conclusion, a chemically controlled doping protocol is reported for obtaining highly efficient Mn doped $CsPbCl_3$ nanocrystals. Using RNH_3Cl as the active chlorinating agent for activating the reactivity of $MnCl_2$ along with $PbCl_2$ at elevated temperature, the doped nanocrystals were synthesized where the Mn d-d emission intensity wastuned as a function of amount of RNH_3Cl. As a consequence, only 5 to 10% Mn(II) precursor became enough in obtaining the highquality doped nanocrystals Analysis suggested that RNH_3Cl helped in controlling the size by increasing the number of particles which provided opportunity for more Mn to react and got doped. Further, varying Cs to Pb precursor concentration, doped 2D platelets were synthesized which also retained the Mn emission. These suggest that beyond the dopant-host precursors concentrations, manipulation of the doping activating reagent can controllably tailor the dopant emission intensities in perovskite host nanocrystals.

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Keywords: $CsPbCl_3$ • d-d emission • doped perovskites • Mn:$CsPbCl_3$ • platelets

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Layout 1:

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Programming Perovskite doping: Controlled doping of Mn(II) in $CsPbCl_3$ nanocrystals were performed by using alkylamine hydrochloride (RNH_3Cl) as doping promoting reagent. The dopant emission intensity is tailored as a function of Mn doping governed by the amount of introduced RNH_3Cl. This helped in stabilizing and also controlling the size of $CsPbCl_3$ nanocrystals which in turned facilitated efficient doping.

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