Electronic Supplementary Information

Suppressed Mn²⁺ Doping in Organometal Halide Perovskite

Nanocrystals by Formation of Two-Dimensional (CH₃NH₃)₂MnCl₄

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1. Experimental

Materials

Lead (II) chloride (PbCl₂, 99%), lead (II) bromide (PbBr₂, 99%), manganese (II) chloride (MnCl₂, 98%), *n*-octylamine (OAm, \geq 99%), oleylamine (OIAm, \geq 99%), dodecylamine (DDAm, \geq 99%), and octadecylamine (ODAm, \geq 99%) were purchased from Sigma-Aldrich and used without any further purification. Toluene (99%), and *N*,*N*-dimethylformamide (DMF, 99.5%) were received from Daechung Chemicals & Metals. Methylammonium chloride and bromide (CH₃NH₃Cl and CH₃NH₃Br) were synthesized by the previously reported methods.

Synthesis of Mn:CH₃NH₃PbCl₃ nanocrystals (NCs) (MnCl₂:MAPbCl₃)

Mn:CH₃NH₃PbCl₃ NCs were synthesized by reprecipitation process where precursors in DMF were instantly precipitated into toluene containing various surface capping agents. PbCl₂ (0.4 mmol) and CH₃NH₃Cl (0.4 mmol) were dissolved in DMF (10 mL) by stirring for 30 min. PbCl₂ was partially substituted by adding MnCl₂ into the precursor solution to match the composition of CH₃NH₃Pb_xCl₃:Mn_(1-x) (x = 0 to 0.9). To ensure NC formation and prevent their further growth, surface capping agents were introduced into the precursor solution. Long alkyl chains with amine-end groups such as OAm, DDAm, ODAm, and OlAm were used with the concentration of from 0.01 to 0.05 mmol/mL. The precursor solution of 1 mL was injected into toluene (10 mL) and stirred for 1 hour at ambient condition. Mn:CH₃NH₃Pb_xCl₃ NCs were separated from the non-reacted precursors by centrifugation of the NC solution at 8000 rpm for 10 min, and then the precipitate was redispersed in a neat toluene. The NCs were collected by repeating this process three times. The concentration of free Mn²⁺ ions in the supernatant of the

final washing step was confirmed to be less than 0.1 ppm by ICP-AES.

Synthesis of MAPbCl_{3x}Br_{3(1-x)} (x = 0-0.66) NCs (PbCl₂:MAPbBr₃)

PbBr₂ (0.4 mmol) and CH₃NH₃Br (0.4 mmol) were dissolved in DMF (10 mL) by stirring for 30 min. PbBr₂ was partially substituted by adding PbCl₂ (0-100 %) into the precursor solution to match the composition of MAPbCl_{3x}Br_{3(1-x)} (x = 0-0.66). Reprecipitation process for the formation of nanoparticles was performed as described in the above section.

Synthesis of Mn:MAPbCl_{3x}Br_{3(1-x)} (x = 0-0.66) NCs (MnCl₂:MAPbBr₃)

PbBr₂ (0.4 mmol) and CH₃NH₃Br (0.4 mmol) were dissolved in DMF (10 mL) by stirring for 30 min. PbBr₂ was partially substituted by adding MnCl₂ (0-90 %) into the precursor solution to match the composition of Mn:MAPbCl_{3x}Br_{3(1-x)} (x = 0-0.66). Reprecipitation process for the formation of nanoparticles was performed as described in the above section.

Synthesis of Mn:MAPbCl_{3x}Br_{3(1-x)} (x = 0.33-1) NCs (MnCl₂:MAPbClBr₂)

PbBr₂ (0.4 mmol) and CH₃NH₃Cl (0.4 mmol) were dissolved in DMF (10 mL) by stirring for 30 min. PbCl₂ was partially substituted by adding MnCl₂ (0-90 %) into the precursor solution to match the composition of Mn:MAPbCl_{3x}Br_{3(1-x)} (x = 0.33-1). Reprecipitation process for the formation of nanoparticles was performed as described in the above section.

Synthesis of Mn:MAPbCl_{3x}Br_{3(1-x)} (x = 0.66) NCs (MnCl₂:MAPbCl₂Br)

PbCl₂ (0.4 mmol) and CH₃NH₃Br (0.4 mmol) were dissolved in DMF (10 mL) by stirring for 30 min. PbCl₂ was partially substituted by adding MnCl₂ (0-90 %) into the precursor solution to match the composition of Mn:MAPbCl_{3x}Br_{3(1-x)} (x = 0.66). Reprecipitation process for the formation of nanoparticles was performed as described in the above section.

Post treatment of CH₃NH₃PbCl₃ NCs using MnCl₂

Post treatment of CH₃NH₃PbCl₃ NCs for Mn doping was carried out at room temperature under ambient conditions. Mn dopant solution was prepared by dissolving the corresponding amounts of anhydrous MnCl₂ in DMF (1 mL). Mn solution (0.1 mL) was injected into CH₃NH₃PbCl₃ NC dispersion under continuous stirring and kept on stirring for 30 minutes. The Mn to Pb ratio in the final product was varied by adjusting the MnCl₂ concentration in Mnprecursor solution.

Characterization

Absorbance and photoluminescence (PL) of colloidal CH₃NH₃Pb_xCl₃:Mn_(1-x) NCs were measured using Shimadzu UV-2600 and Hitachi F-7000 fluorescence spectrophotometer (λ_{Exc} = 365 nm). A quartz cuvette was used for the absorbance and PL measurements. A periodical PL measurements were conducted for the NCs solution (t = 0-72 hrs) to confirm their timedependent PL stability. Photoluminescence quantum yield (PLQY) was determined based on a comparative method, where 9,10-diphenylanthracene (DPA) was used as a reference (PLQY = 90%). Time-correlated single-photon counting (TCSPC) was used to measure PL decay spectra by Fluorolog-3 (Horiba Scientific) with a laser source at 375 nm. The fluorescent decay curves were fitted by the following tri-exponential fitting,

$$I(t) = C + \alpha_1 exp\left(-\frac{t}{\tau_1}\right) + \alpha_2 exp\left(-\frac{t}{\tau_2}\right) + \alpha_3 exp\left(-\frac{t}{\tau_3}\right)$$

where I(t) is the fluorescent intensity, τ is the lifetime, *C* is the pre-exponential factor. The fitting accuracy (determined by χ^2) was 1 ± 0.2 . Average lifetime ($\tau_{avg.}$) of the fluorescent decay was determined by the average of a tri-exponential decay. Transmission electron micrographs were obtained using field-emission transmission electron microscope (JEM-2100F) operated at 200 kV. X-ray diffraction patterns were measured using Bruker AXS D8 diffractometer with Cu-K α ($\lambda = 1.54$ Å). X-ray photoelectron spectra were collected using Xray photoelectron spectrometer (XPS, K-Alpha⁺, Thermo Fisher Scientific) with a monochromatic X-ray source from Al K α ($h\nu$ = 1486.6 eV). Concentration of Mn²⁺ ion in the CH₃NH₃Pb_xCl₃:Mn_(1-x) NCs and the supernatant after washing step was measured from the NCs (100 mg) dissolved in nitric acid (40 mL) using inductively coupled plasma atomic emission spectroscopy (ICP-AES, Optima 7300 DV).

2. Results

	$\tau_1^{}$, sec	$\tau_2^{}$, sec	$\tau_3^{}$, sec	C	α ₁	α22	α ₃	τ_{avg} , sec	χ^2
MAPbCl ₃	1.65E-05	9.74E-05	3.62E-06	12.5	1796	110	3579	2.97E-05	1.3002
Mn:MAPbCl ₃ (10%)	1.06E-03	1.66E-03	2.31E-04	6.95	4396	3740	1615	1.36E-03	1.0799
Mn:MAPbCl ₃ (50%)	8.44E-04	2.37E-04	1.56E-03	1.37	2076	626	2282	1.29E-03	1.1174
Mn:MAPbCl ₃ (90%)	5.89E-04	1.25E-03	1.33E-04	3.29	2858	1702	1590	9.17E-04	1.1626

Table S1. Parameters used to fit the PL decay curves of the $Mn^{2+}:MAPbCl_3 NCs$.

	PLQY (%)							
$\operatorname{MinCl}_2(\%)$	<i>n</i> -octylamine (OAm)	oleylamine (OlAm)	dodecylamine (DDAm)					
1	0.2	0.2	0.1					
2	1.7	0.4	0.2					
5	0.8	0.9	0.4					
10	1.2	1.9	0.6					
20	1.2	3.1	0.5					
50	4.4	7.2	2.8					
70	2.6	4.5	3					
90	1.6	1.7	2.5					

Table S2. PLQY (%) of the Mn^{2+} :MAPbCl₃ NCs depending on the type of surface ligands.



Figure S1. TEM images of (a) undoped and (b, c) Mn^{2+} -doped MAPbCl₃ by adjusting the MnCl₂ concentration: (b) 10% and (c) 50%.



Figure S2. High-resolution XPS spectra of (a) C 1s, (b) Cl 2p, (c) Mn 2p, and (d) Pb 4f for Mn²⁺-doped MAPbCl₃ NCs.



Figure S3. XRD patterns of (a) Mn^{2+} -doped MAPbCl_{3x}Br_{3(1-x)} (x = 0-0.33) NCs and (b) Mn^{2+} -doped MAPbCl_{3x}Br_{3(1-x)} (x = 0.33-0.66) NCs by adjusting the MnCl₂ concentration (0-50 %).



Figure S4. Dependence of the PL emission on the relative halogen anion contents of Mn²⁺-doped MAPbCl_{3x}Br_{3(1-x)} NCs. (a) Normalized PL spectra of the undoped MAPbCl_{3x}Br_{3(1-x)} (x = 0-0.66) NCs exhibiting a blue shift with Cl contents and Mn²⁺-doped MAPbCl_{3x}Br_{3(1-x)} NCs with the various Cl to Br ratio. (b) Ratio of the PL intensity of the Mn²⁺- and band-edge emission (PL_{Mn}/PL_{Exciton}) for the respective MAPbCl_{3x}Br_{3(1-x)} (x = 0-1) NCs as a function of the MnCl₂ contents in the precursors. (c) Dependence of maximum PL_{Exciton} emission wavelength (λ_{Max}) on Cl contents for the respective MAPbCl_{3x}Br_{3(1-x)} (x = 0-1) NCs. Excitation wavelength (λ_{Exc}) was fixed at 365 nm. The dashed line is a guide to the eye.



Figure S5. Steady-state absorption spectra of (a) the undoped MAPbCl_{3x}Br_{3(1-x)} (x = 0-0.66) NCs and (b-d) Mn²⁺-doped MAPbCl_{3x}Br_{3(1-x)} NCs with various Cl to Br ratio depending on dopant (MnCl₂) concentration. The molar ratio (x) is in the range of (b) 0-0.66, (c) 0.33-1, and (d) 0.66, respectively.



Figure S6. Photoluminescence of Mn^{2+} -doped MAPbCl₃ (0-90%) NCs containing (a) dodecylamine (DDAm), (b) octadecylamine (ODAm), and (c) oleylamine (OlAm). The inset shows the photo images of corresponding samples under UV illumination ($\lambda_{ex} = 365$ nm).



Figure S7. (a) Dependence of PLQY (%) of $Mn^{2+}:MAPbCl_3$ on the contents of $MnCl_2$ (%) for OAm, DDAm, and OlAm. (b) Time-dependent PL stability of $Mn^{2+}:MAPbCl_3$ (50%) NCs ($\lambda_{ex} = 365$ nm).



Figure S8. Photoluminescence and optical absorbance of Mn^{2+} -doped MAPbCl₃ (0-50 %) NCs by post treatment