Supporting Information

Coupled Halide-deficient and Halide-rich Reaction System for Doping in Perovskite Armed Nanostructures

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EXPERIMENTAL SECTION

Materials and Methods

Materials: 1-octadecene (ODE, tech, 90%), oleic acid (OA, tech, 90%), oleylamine (OLA, tech, 70%), manganese (II) acetate tetrahydrate ($Mn(OAc)_2.4H_2O$, 99.999%) and lead (II) chloride ($PbCl_2$, 99.999%) were purchased from Sigma-Aldrich. Cesium carbonate (Cs_2CO_3, 99%) and hydrochloric acid (HCl, 35wt % in H_2O) were purchased from Spectrochem, India. All reagents were used as received without further purification.

Preparation of Cs-oleate precursor: In a typical synthesis, Cs_2CO_3 (0.2175 g, 0.67 mmol), OA (0.85 mL) and ODE (5.9 mL) were loaded into a 25 ml 3-neck flask. The solution was purged with N_2 for 2h at 120 °C. Then the temperature was increased to 150 °C and annealed at that temperature for 15 min. The resulting mixture was collected under hot condition and stored in previously deaerated vial. Since Cs-oleate precipitates out of ODE at room-temperature, it must be preheated to 100 ^oC before use.

Preparation of OLA-HCl stock solution: 1.7 mL of OLA and 0.134 mL of HCl were taken in a 25 mL three necked round bottom flask and the solution was purged with N_2 for 2h at 120 °C with high gas flow to remove moisture and water content from the reaction medium. The resulting mixture was collected under hot condition and stored in previously deaerated vial. The stock solution of OLA-HCl becomes solid in room temperature and hence, further heating to ~ 80 ^oC is required before injecting to reaction system.

Synthesis of Mn(II) doped $CsPbCl_3$ seed clusters: Seed clusters were synthesized following some modification to our previous reported method.[1] In a typical synthesis of Mn doped $CsPbCl_3$ seed nanoclusters, lead chloride (0.056 g, 0.2 mmol), manganese acetate tetrahydrate ($Mn(OAc)_2.4H_2O$)(0.049 g, 0.2 mmol), oleic acid (OA, 0.5 mL), oleylamine (OLA, 0.5 mL) were taken along with 1-octadecene (ODE, 3.5 mL) in a 25 mL three necked round bottom flask. The reaction mixture was then deaerated with N_2 for 1 h at 120 °C until all the precursors dissolved to give a clear yellowish solution. Then the temperature was lower down to 35 °C and 0.25 mL of Cs-oleate stock solution was injected into the reaction system. The reaction mixture was

annealed at that temperature for another 30 min. The resulting mixture was centrifuging at 6000 rpm for 10 min. After centrifugation, the supernatant was discarded and the precipitate was obtained. Finally, 1 mL ODE was added to disperse the precipitate. It was important to keep the seed solution under 18 ^{o}C (in refrigerator) before further use.

Synthesis of Mn(II) doped $CsPbCl_3$ hexapod nanocrystals: Hexapod structures were synthesized adopting our previous reports.[1] In a typical synthesis, 3.5 mL ODE was taken in a 25 mL three necked round bottom flask and the solution was degassed for 15 min at 120 ^{o}C with purging N_2. Then the flask was heated to 280 °C and 1.0 mL above-mentioned seed cluster solution (Mn doped $CsPbCl_3$ seed cluster) was swiftly injected and annealed for 5 min. Then, 0.5 mL of stock OLA-HCl solution was introduced. The reaction was further annealed for 5 minutes and after that the heating mantle was removed and allowed to cool down naturally. The nanocrystals were harvested by centrifuging at 6000 rpm for 10 min, discarding the supernatant and then redispersing the nanocrystals in hexane.

Synthesis of Mn(II) doped nanoplatelets: For nanoplatelets synthesis, the seed clusters were injected at high temperature in presence of excess halide. In a typical synthesis, 3.5 mL ODE was taken in a 25 mL three necked round bottom flask and the solution was degassed for 15 min at 120 ^{o}C with purging N_2. Then the flask was heated to desired temperature (180-280 ^{o}C) and 0.5 mL of stock OLA-HCl solution was added. Soon after that 1.0 mL of above-mentioned seed cluster solution (Mn doped $CsPbCl_3$ seed cluster) was swiftly injected and annealed for another 5 min. Then the heating mantle was removed and allowed to cool down naturally. The nanocrystals were harvested by centrifuging at 6000 rpm for 10 min, discarding the supernatant and then redispersing the nanocrystals in hexane.

Synthesis of Mn(II) doped nanocubes: For nanocube synthesis, the seed clusters were injected at high temperature in ODE without any other additives. In a typical synthesis, 3.5 mL ODE was taken in a 25 mL three necked round bottom flask and the solution was degassed for 15 min at 120 ^{o}C with purging N_2. Then the flask was heated to desired temperature (180-260 ^{o}C) and 1.0 mL of above-mentioned seed cluster solution (Mn doped $CsPbCl_3$ seed cluster) was swiftly injected and annealed for another 5 min. Then the heating mantle was removed and allowed

to cool down naturally. The nanocrystals were harvested by centrifuging at 6000 rpm for 10 min, discarding the supernatant and then redispersing the nanocrystals in hexane.

Characterizations

Electron Microscopic Measurements: Transmission Electron Microscopic (TEM) and Scanning Transmission Electron Microscopic (STEM) characterizations were carried out on a JEOL-JEM-F200 electron microscope with an accelerating voltage of 200 kV. Energy-dispersive spectroscopic (EDS) measurements were also performed using the same instrument. Samples for the imaging and EDS measurements were prepared by dropping a drop of dilute solution of nanocrystals in hexane on carbon coated copper grid purchased from Ted Pella, the grids were dried in air overnight and stored in a vacuum desiccator.

Optical Property Measurements: Photoluminescence (PL) spectra were recorded on a Horiba Jobin Yvon-Fluoromax-4 spectrophotometer and UV-Vis absorption spectra were recorded on an Agilent-cary 60 spectrophotometer. Photoluminescence Quantum Yield (PLQY) was measured using Horiba Quanta Phi integrated sphere fitted with the same Fluromax instrument. Samples for quantum yield measurements were prepared by drop casting a thin film of the nanocrystals on glass slides. Excited state lifetime of the doped samples were measured using a Horiba Yobin (DeltaFlex-01) time correlated single photon counting spectrometer.

Powder X-ray Diffraction (XRD) Measurements: Brukar Advance D8 diffractometer, using Cu K_{α}(λ= 1.54 Å) as the incident radiation, was employed for obtaining the powder diffraction patterns. Samples were prepared by drop casting a film of the nanocrystals on glass slides.

Electron Paramagnetic Resonance (EPR) Measurement: EPR measurement was carried out on a 9.5 GHz Bruker ESP-300 spectrometer operated at X-band frequency. Solid sample was taken in EPR tube for measurement and measurement was performed at room temperature (25 ^{o}C).

SUPPORTING FIGURES

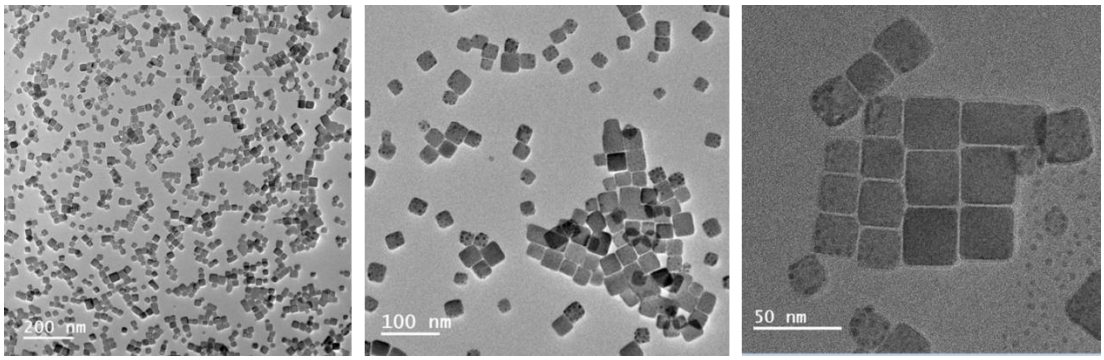


Figure S1. TEM images of $CsPbCl_3$ nanocubes after OLA-HCl treatment at 260 °C. After the synthesis of nanocubes at 260 °C, 0.5 mL of OLA-HCl was injected and annealed for another 5 min at that temperature.

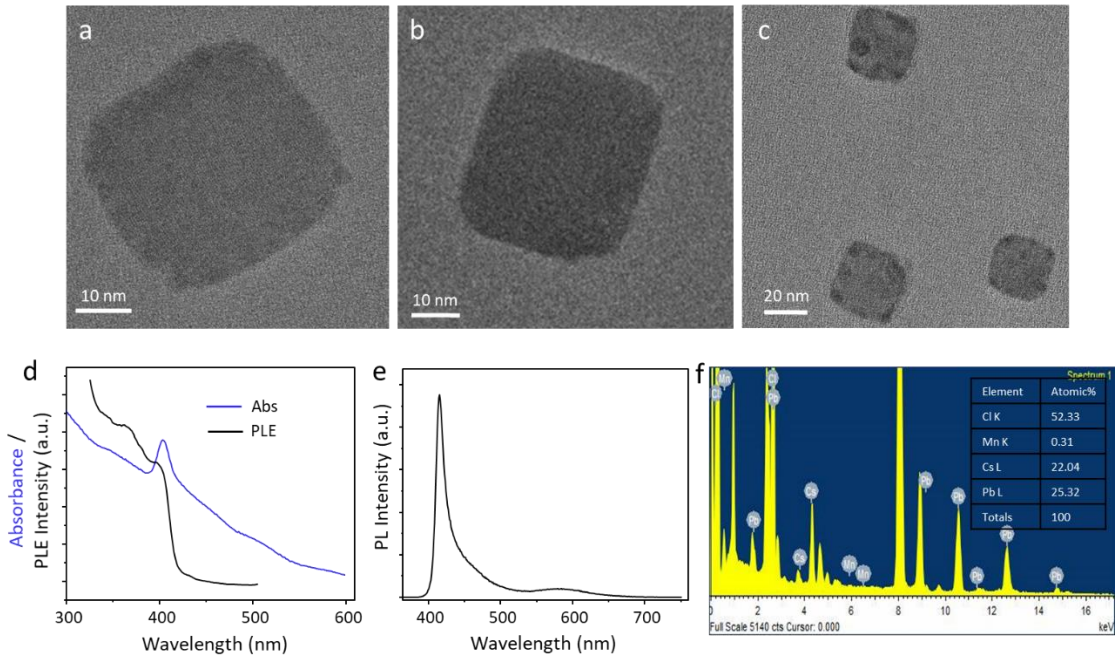
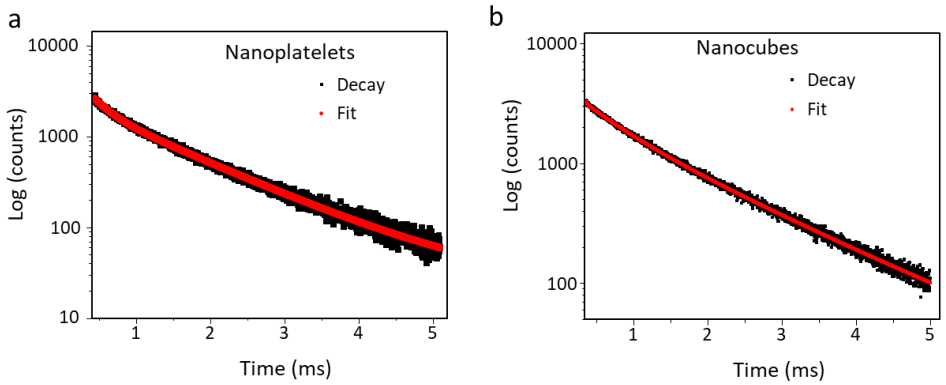


Figure S2. (a-c) TEM images of the Mn doped $CsPbCl_3$ polyhedron shaped nanocrystals obtained from the 280 °C reaction without OLA-HCl. (d) Absorption/PLE, (e) PL and (f) EDS spectra with atomic percentage of the same nanostructure. Excitation wavelength for PL measurement was 350 nm and PLE was measured at 585 nm.



c

Sample	T1 (ms)	T2 (ms)	B1 (Relative amplitude %)	B2 (Relative amplitude %)	Chi sq.	Average lifetime (ms)
Nanocubes	0.365285 ±0.03452	1.133471 ±0.0136169	10.04	89.96	1.099165	1.0539 ± 0.037117
Nanoplates	0.531408 ± 0.0356404	1.8349 ± 0.0130674	29.65	70.35	1.051359	0.867808 ± 0.03796

Figure S3. Excited state decay lifetime plots of (a) nanoplates, (b) nanocubes of $CsPbCl_3$ nanostructures and (c) corresponding values of the fitted parameters. Equation used for fitting is A+ B1*exp(-i/T1) + B2*exp(-i/T2). Excitation wavelength was 365 nm and emission lifetime was measured at 590 nm.

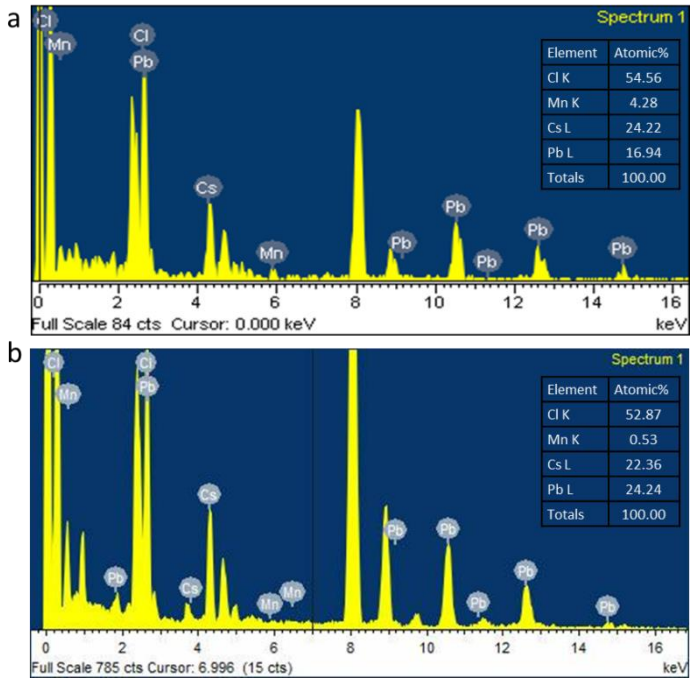


Figure S4. Energy-dispersive spectra (EDS) and atomic percentages of elements obtained from (a) Mn doped nanoplatelets and (b) Mn doped nanocubes of $CsPbCl_3$.

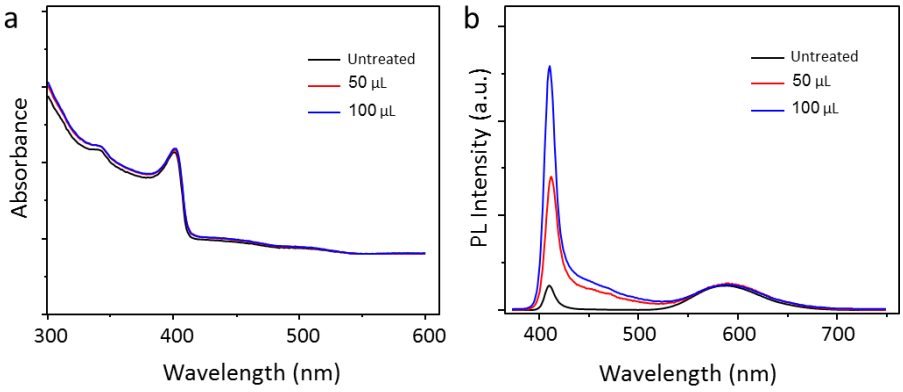


Figure S5. (a) UV-Vis absorption and (b) photoluminescence (PL) spectra of Mn doped nanocubes after different amount of OLA-HCl treatment at room temperature. Excitation wavelength was 350 nm. OLA-HCl treatment was performed by preparing an OLA-HCl stock in hexane and then subsequently adding desired amount of the stock solution to the nanocube solution directly in the cuvette. The OLA-HCl stock solution for this experiment was prepared by diluting 0.1 mL of the 0.01 M OLA-HCl in ODE in 1mL hexane.

SUPPORTING TABLE

Table S1. Table of the values of the parameters obtained after fitting the decay lifetime plot. Equation used for fitting is A+ B1*exp(-i/T1)+ B2*exp(-i/T2)

T1 (ms)	T2 (ms)	B1 (Relative amplitude %)	B2 (Relative amplitude %)	Chi sq.	Average lifetime (ms)
0.235349 ± 0.0260337	1.19679 ± 0.0125196	8.46	91.54	1.11632	0.889458 ± 0.02888

REFERENCE

(1) Peng, L.; Dutta, S. K.; Mondal, D.; Hudait, B.; Shyamal, S.; Xie, R.; Mahadevan, P.; Pradhan, N. Arm Growth and Facet Modulation in Perovskite Nanocrystals. *J. Am. Chem. Soc.* **2019**, *141*, 16160-16168.