Electronic Supporting Information (ESI) for:

$CsPbX_3/Cs_4PbX_6$ core/shell perovskite nanocrystals

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1. Chemicals

Lead (II) bromide ($PbBr_2$, 99.999% trace metals basis), Lead (II) chloride ($PbCl_2$, 99.99% trace metals basis), Lead (II) iodide (PbI_2, 99.99% trace metals basis), cesium carbonate (Cs_2CO_3, 99.9% trace metals basis) and oleylamine (OLA, technical grade, 70%) were purchased from Sigma-Aldrich. 1-Octadecene (ODE, technical grade, 90%) and zinc bromide ($ZnBr_2$, anhydrous, 99.5%) were purchased from J&K Scientific. Oleic acid (OA, A.R.) was purchased from Macklin. Hexane (analytical grade, 95%) was purchased from Beijing Chemical Works.

2. Synthesis of $CsPbBr_3/Cs_4PbBr_6$ core/shell NCs

Cs-oleate was prepared firstly. In detail, Cs_2CO_3 (1.25mmol), ODE (20 mL) and OA (1.55 mL) were loaded into a 50 mL 3-neck flask, attached a Schlenk Line, degassed the mixture at 100 °C for 30 min under vacuum, and then heated to 150 °C under N_2 for 30 min. The Cs-oleate solution was stored by stirring at 100 °C to avoid precipitation.

Synthesis of $CsPbBr_3$ NCs was performed according to the method slightly modified from the protocol reported by Protesescu et al. Briefly, $PbBr_2$ (0.188 mmol), ODE (5 mL), OA (0.5 mL) and OLA (0.5 mL) were mixed in a 50 mL 3-neck flask, heated to 100 °C and purged under vacuum for 30 min. Then, the temperature was increased to 170 ºC and 0.058 mmol Cs-oleate solution was quickly injected. The reaction mixture was cooled with the water bath in 10 seconds.

Synthesis of $CsPbBr_3/Cs_4PbBr_6$ core/shell NCs was performed by using the above solution containing $CsPbBr_3$ NCs without any treatment. Before the growth of the Cs_4PbBr_6 shell, the resulting $CsPbBr_3$ NCs solution was lowered to room temperature and 0.1 mmol (or 0.2 mmol) $ZnBr_2$ was added to the flash, degassed at 50 °C for 20 min under vacuum. Afterward the temperature was raised to 70 °C under a nitrogen atmosphere, Cs-oleate with different amount (for instance, 0.203 mmol corresponding to a shell thickness of 1.5 nm) was quickly injected. The solution was lowered to room temperature using a water bath after 3 min. The solution turned bright green again.

To collect the NCs, the crude solution was then centrifuged at 8000 rpm for 5 min. After centrifugation, the supernatant was discarded and the NCs were re-dispersed in 1 mL hexane.

After centrifuging the suspension (3 min, 3000 rpm), the supernatant was saved for further investigation. $CsPbCl_3/Cs_4PbCl_6$ and $CsPbI_3/Cs_4PbI_6$ core/shell NCs were prepared following the same procedures, except different halide source.

3. Synthesis of pure Cs_4PbBr_6 NCs for comparison

The Cs_4PbBr_6 NCs were synthesized according to a reported method with slight modifications, i.e. the amount of Cs-oleate and the temperature. $PbBr_2$ (0.2 mmol) was first added to a mixture of ODE (8 mL), OA (0.4 mL) and OLA (2 mL) in a 50 mL reaction flask. The mixture was degassed for 30 min at 100 °C. Then the solution was allowed to cool down under N_2. When the temperature reached 70 °C，0.46 mmol of Cs-OA (0.325 g Cs_2CO_3 dissolved in 5 mL OA in a 50 ml 3-neck flask，the details were the same as preparation of Cs-oleate) was swiftly injected. After 3 min, the solution was quickly cooled down using a water bath.

4. Characterization

TEM images of obtained NCs were acquired by a JEM-2100 transmission scanning electron microscope (TEM, JEOL, Japan). UV−vis spectra were recorded using a JASCO V-570 spectrophotometer at room temperature. Fluorescence measurements were carried out on a Cary Eclipse fluorescence spectrophotometer (Varian, Inc.). X-ray diffraction (XRD) measurements were performed on a D8 Focus X-ray diffractometer.

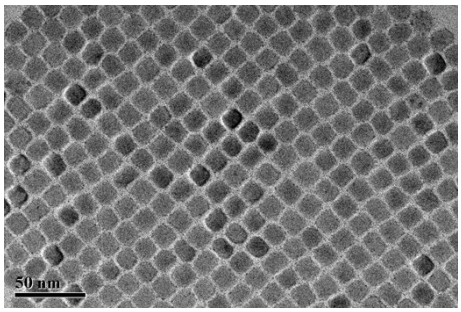

Figure S1, TEM image of pure Cs_4PbBr_6 NCs.

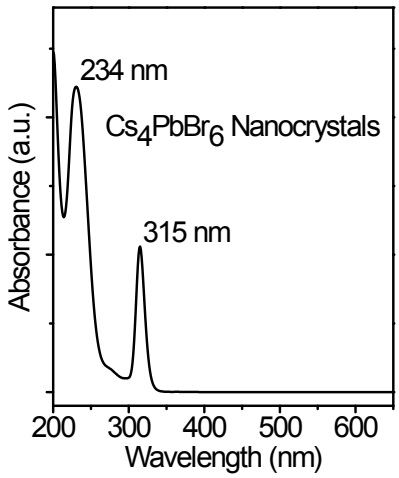

Figure S2, Absorption spectra of pure Cs_4PbBr_6 NCs.

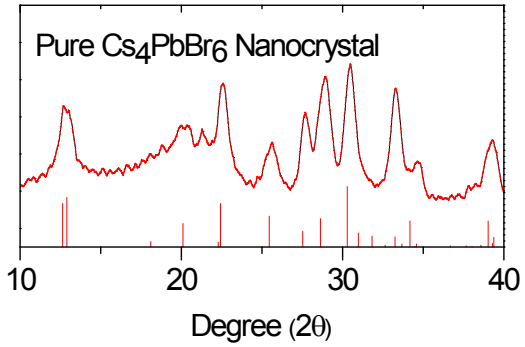

Figure S3, XRD patterns of pure Cs_4PbBr_6 NCs.

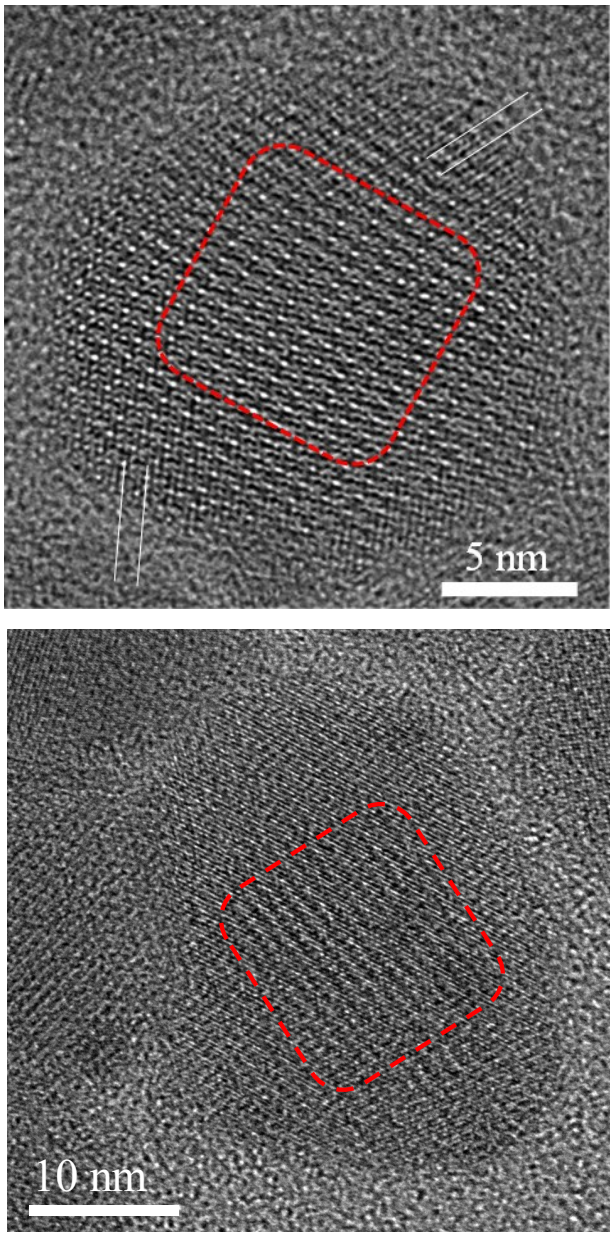

Figure S4, HRTEM image of $CsPbBr_3/Cs_4PbBr_6$ core/shell NCs.

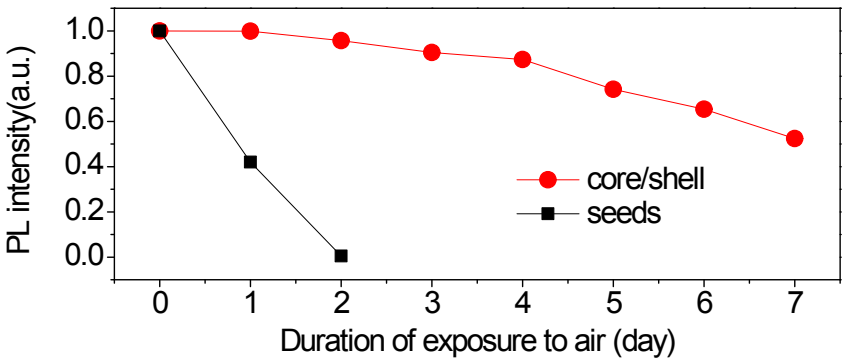

Figure S5, PL intensity of $CsPbI_3$ NCs (Black Square) and $CsPbI_3/Cs_4PbI_6$ core/shell NCs (Red sphere) exposed to air as function of time over one week.