Supporting Information

Design principle of all-inorganic halide perovskite-related nanocrystals

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Experimental Section

Materials: PbBr₂ (99.999%), N,N-dimethylformamide (DMF, AR, 99.5%), oleic acid (OA, 85%) and oleylamine (OLA, 80-90%) were purchased form Aladdin. CsBr (99.999%) was purchased from Aldrich. Toluene (analytical pure, AR) and ethyl acetate (AR) were obtained from Sinopharm Chemical Reagent Co., Ltd. All reagents were used directly without further purification.

Preparation of precursors: A series of precursors were prepared according to the following steps. Different amounts of $PbBr_2$ and CsBr were dissolved into 10 ml of DMF at room temperature; then 1 ml of OA and 0.5 ml of OLA were introduced into the solution under strong magnetic stirring.

Synthesis of all-inorganic perovskite halide (AIPH)-related nanocrystals: All-inorganic perovskite halide (AIPH)-related (e.g., CsPbBr₃, Cs₄PbBr₆, and CsPb₂Br₅) nanocrystals were synthesized through a modified room temperature saturated recrystallization (RTSR) method. In a typical experiment, 0.7 ml of the solutions were injected into 10 ml of toluene under vigorous magnetic stirring. The nanocrystals were first centrifuged out from the liquid phase at 8000 rpm after reacting for 10 s, then washed twice using a mixture of toluene and ethyl acetate at a volume ratio of 1:1 without specification. Thus obtained samples were re-dispersed into toluene for storage and further characterizations.

Characterization: X-ray diffraction patterns were recorded using an X-ray diffractometer with Cu K α radiation ($\lambda = 1.54178$ Å) as X-ray source (PANalytical). UV–vis absorption spectra were obtained using an UV-2600 absorption spectrophotometer (Shimadzu). Photoluminescence (PL) and PL excitation spectra were measured using a FLS920 dedicated fluorescence spectrometer (Edinburgh Instruments). Transmission electron microscopy (TEM) analysis was carried out with a Tecnai G2 F20 S-TWIN TEM (FEI Company).



Figure S1 TEM image of Cs_4PbBr_6 nanocrystals synthesized at $C_{PB}:C_{CB} = 0.25$ ($C_{CB} = 0.04$ M). The size of the Cs_4PbBr_6 nanocrystals ranges from 80 nm to 350 nm with a poor dispersibility.



Figure S2 PL and UV-Visible absorption spectra of the product synthesized at $C_{PB}:C_{CB} = 0.25$. No obvious PL signal was obtained, indicating that $C_{S_4}PbBr_6$ can not emit light in the visible wavelength range.



Figure S3 PL and UV-Visible absorption spectra of the product obtained at C_{PB} : $C_{\text{CB}} = 5$.



Figure S4 (a) TEM and (b) SAED characterization of the ultrafine spherical $CsPb_2Br_5$ nanocrystals. Insert in (a): High-resolution TEM image.



Figure S5 Pure CsPbBr₃ nanocrystals fabricated by injecting 70 μ l of DMF composed of an equal amount of PbBr and CsBr at a concentration of 0.04 M into 10 ml of toluene. (a) XRD pattern. Olive lines marked the position of the standard XRD peaks of CsPbBr₃ (PDF No. 180364). (b) TEM image.