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Supporting Information

Revisit the nanocrystal formation process of zero-dimensional

perovskite

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Experimental Section

Materials:

All reagents were used as received without any purification: cesium carbonate (Cs₂CO₃, 99%), cesium acetate (CsAc,99.99%), oleic acid (OA, 90%), lead bromide (PbBr₂, 99%), 1-propanol (1-PrOH), octylamine (OcAm, 99%), octanoic acid (OcAc, 99%) and hydrobromic acid (HBr, 48 wt% in water) were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd., China. N-hexane (n-hex, 99.5%) and N, N-dimethylformamide (DMF, 99.5%) were purchased from Tianjin Fuyu Fine Chemical Co., Ltd., China. The oleylamine (OLA, 80 - 90%) was purchased from Shanghai Macklin Biochemical Co., Ltd., China and toluene (99.5%) was purchased from Yantai Far East Fine Chemical Co., Ltd., China.

Synthesis of Cs-oleate Precursor:

Typically, 2.25 g of Cs_2CO_3 and 21.5 mL of OA were loaded in a 50-mL three-necked bottle, followed by heating up to 120 °C under vigorous stirring in vacuum. The reaction was allowed to proceed for 1 hour before naturally cooling down to room temperature. The yellow clear Cs-oleate precursor solution was kept in a vial for further use.

Synthesis of Cs₄PbBr₆ Nanocrystals:

Cs₄PbBr₆ nanocrystals were synthesized using a modified reverse microemulsion method.^{1, 2} Typically, 0.2 mL Cs-oleate precursor, 10 mL n-hex, 5 mL OA were loaded in a 20-mL vial under vigorous stirring to form a Cs-precursor. Then, an admixture of PbBr₂ (0.03 M, DMF, 0.95 mL), HBr (48 wt%, 15 μ L), 0.1 mL OA, and 0.05 mL OLA was thoroughly vortexed and swiftly injected into above precursor under vigorous stirring. The reaction was allowed to proceed for 10 minutes at ambient condition, after which a green colloid of Cs₄PbBr₆ nanocrystals was formed. The nanocrystals were collected by centrifugation at 4000 rpm for 5 minutes, and the pellet was dispersed in 1-mL toluene for further characterization.

Synthesis of CsPbBr₃ Nanosheets:

Firstly, CsAc (32 mg), 1-PrOH (3 mL) and n-Hex (6 mL) were added into a 20 mL

vial and stirred under air condition until a transparent solution was formed. Then, PbBr₂ (305.8 mg), 1-PrOH (0.56 mL), OcAc (0.56 mL) and OcAm (0.56 mL) were added into a 10 mL vial and heated at 90 C in air under vigorous stirring. After the PbBr₂ salt dissolved completely, the hot solution was quickly injected into the prepared CsAc solution under vigorous stirring at ambient condition. Immediately, the color of the mixture turned green, and the reaction completed in 2 min. Finally, the mixture was centrifuged at 4,000 rpm, and the precipitate of nanosheets was dispersed in toluene.

X-ray Diffraction:

X-ray diffraction patterns were collected using an X-ray diffractometer (Rigaku Ultima IV) coupled with Cu-K α radiation ($\lambda = 1.5406$ Å), with a scanning rate at 10 °/min and step size of 0.02°.

Transmission Electron Microscopy (TEM):

TEM and high-resolution transmission electronic microscopy (HRTEM) images were obtained using a transmission electron microscope (JEM-2100 plus, JEOL) under an acceleration voltage of 200 kV. Low-dose HRTEM images were acquired by a Gatan K2 direct-detection camera operated in electron-counting mode (camera counting frame rate of 400 fps (frames per second) at 4 k \times 4 k resolution) with a final image output rate of 40 fps at 4 k \times 4 k resolution. The electron dose was set at 1 e·A^{-2·}s⁻¹. An exposure of 3 s therefore results in an image stack of 120 individual image frames. These frames can be summed to improve the signal-to-noise ratio (SNR).

Steady-State Measurements of Photoluminescence and Absorption:

 Cs_4PbBr_6 NCs colloid in toluene were transferred to a quartz cuvette for steady-state PL and absorption spectral measurement. A spectrometer (FS5, Edinburgh Instruments) with a xenon lamp was used to record the photoluminescence spectra. The excitation wavelength was set at 365 nm, and PL was recorded with step size of 1 nm and dwell time of 0.2 s. A UV-vis spectrophotometer (EVOLUTION 201, Thermo Scientific Corporation) measurements in the range of 300 - 600 nm.



Figure S1. The photograph of the in-situ PL monitoring system. The reaction was conducted in the quartz cuvette, where a 405-nm laser beam (44 mW) was directed to excite the emitters formed inside. The PL was collected perpendicularly by a fiber optic spectrometer (Aurora 4000, GE-UV-NIR, Changchun New Industries Optoelectronics Tech. Co., Ltd). The time interval of collecting spectrum was 200 ms. The data acquisition was initiated before reaction to ensure a complete recording of the whole reaction from beginning.



Figure S2. (a) The in-situ PL spectra evolution with time (0 - 360 s) when setting the reaction at 293 K. The enlarged figure of varied period at (b) 0 - 1 s, (c) 1 - 6 s and (d) 6 - 360 s.



Figure S3. (a)The evolution of the in-suit PL spectra of 3D CsPbBr₃ NCs over time (0 - 30 s). The spectra rose rapidly in 0 - 5 s, and only slightly changed in 5 - 30 s. (b) Evolution of PL position and integrated PL intensity with time.



Figure S4. The change of PL peak position in nucleation and growth process at 293K showed a continuous redshift.



Figure S5. TEM images of intermediate states of nanocrystals at varied reaction times (6, 60, 180, and 360 s) in stage II.



Figure S6. (a) Size evolution histogram of "black spots". (b) Number evolution histogram of "black spots".



Figure S7. (a) The in-situ PL spectra evolution with time (0 - 400 s) when setting the reaction at 268 K. The enlarged figure of varied period at (b) 0 - 5 s, (c) 5 - 30 s and (d) 30 - 400 s.



Figure S8. (a) The in-situ PL spectra evolution with time (0 - 600 s) when setting the reaction at 258 K. The enlarged figure of varied period at (b) 0 - 13 s, (c) 13 - 63 s and (d) 63 - 600 s.



Figure S9. The evolution of PL intensity at 268 K (a) and 258 K (b) with reaction time, showing a similar trend to the case at 293 K.

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