Supporting Information

A New Method to Discover Reaction Mechanism of Perovskite Nanocrystals

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Experimental Section

Chemicals: Cs₂CO₃ (99.9%), iodotrimethylsilane (95%), bromotrimethylsilane (97%), chlorotrimethylsilane (99%) and CH₃COOCs (99.9%) were attained from J&K. Oleic acid (90%, OA), octadecene (90%, ODE), PbO (99.0%) and Lead stearate (99.9%, PbSt₂) were purchased from Alfa Aesar. Oleylamine (80-90%, OLA), (CH₃COO)₂Pb (99.99%) and Pb(NO₃)₂ (99.99%) were purchased from Aladdin. Hexane (99.5%) was obtained from Beijing Chemical Factory. PbO (99.0%) was attained from Sigma-Aldrich. All the chemicals were used without further purification.

Synthesis CsPbBr₃ NCs: 10 mL ODE, 1mL OA, 1 mL OLA, 0.1mmol Cs₂CO₃ and 0.2 mmol PbSt₂ were loaded into a 50 mL three-neck round-bottom flask, degassed under vacuum for 10 min and dried under vacuum for 1 h at 120°C. Then, the temperature was elevated to 180°C under N₂ protection and 0.08 mL TMSBr was quickly injected.
5 seconds later, an ice-water bath was applied to cool down the solution to room temperature. Next, the as-prepared solution was centrifuged at 7000 rpm for 10 min. Hexane was added to the precipitate, and then centrifuged at 7000 rpm for 2 min. Finally, the NCs were acquired in the supernatant. The amount of Cs$_2$CO$_3$, PbSt$_2$ and TMSBr can be adjusted at will, for example, Cs$_4$PbBr$_6$ NCs were synthesized under 0.05 mmol PbSt$_2$. Besides, other Cs and Pb monomers can also be used to synthesis perovskite NCs, such as PbO, (CH$_3$COO)$_2$Pb, CH$_3$COOCs et al. For the mixed halide perovskite NCs, certain feed ratio of halosilanes (TMSBr, TMSI or TMSCl) were mixed previously with 0.5 ml ODE, then the mixture was vibrated 3 minutes and injected into the Cs and Pb solution.

**Characterizations:** Fluorescence emission spectra were measured using an Ocean Optics spectrometer. Absorbance spectra of samples were carried out by using a Shimadzu UV-2550 spectrophotometer. The morphology of the NCs was observed by a FEI Tecnai G2 Spirit TWIN transmission electron microscope (TEM) operating at 100 kV. X-ray diffraction (XRD) patterns of NCs were acquired using a Bruker D8 Advance X-ray diffractometer (Cu Kα: λ = 1.5406 Å). Fourier transform infrared spectroscopy (FTIR) was performed on a Thermo-Nicole iS50 FTIR-spectrometer. The absolute PL QYs of the samples were obtained by a fluorescence spectrometer (FLS920P, Edinburgh Instruments) equipped with an integrating sphere with its inner face coated with BENFLEC. Time-resolved PL lifetime measurements were carried out using a time-correlated single-photon counting (TCSPC) lifetime spectroscopy system with a picosecond pulsed diode laser (EPL-380 nm) as the single wavelength excitation light source. The absolute PL quantum yields of samples were determined by standard procedures using a fluorescence spectrometer (FLS920P, Edinburgh Instruments) equipped with an integrating sphere. Atomic force microscopic (AFM) experiments were performed with an Agilent series 5100 AFM/STM. Nuclear Magnetic Resonance (NMR) measurements were recorded on a Bruker Avance 400 Spectrometer operating at a $^1$H frequency of 400 MHz.
Figure S1. TEM image of Cs$_4$PbBr$_6$ perovskite QDs; (b) size distributions of histogram of these QDs in (a); (c) HRTEM image of Cs$_4$PbBr$_6$ QDs; (d) SAED pattern Cs$_4$PbBr$_6$ QDs (e) Schematic of the cubic Cs$_4$PbBr$_6$ perovskite lattice.

Figure S2. TEM image of the mixture CsPbBr$_3$ and Cs$_4$PbBr$_6$ QDs with a Cs:Pb:Br ratio of 1:0.7:3.
Figure S3. AFM image (a) of the mixture CsPbBr$_3$ and Cs$_4$PbBr$_6$ QDs with a Cs:Pb:Br ratio of 1:0.7:3 and (b) the height distribution.

Figure S4. EDX spectrum of CsPbBr$_3$ QDs.

<table>
<thead>
<tr>
<th>Reaction ratio of Cs:Pb:Br</th>
<th>1:0.25:3</th>
<th>1:0.7:3</th>
<th>1:1:3</th>
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<tr>
<td>Final ratio of Cs:Pb:Br</td>
<td>3.8:1:5.7</td>
<td>1.2:1:3.7</td>
<td>0.85:1:3.1</td>
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Table S1. Element ratio acquired from EDX.
Figure S5. Mapping images of CsPbBr$_3$ QDs. (a) High-angle annular dark-field scanning TEM (HAADF-STEM) image of CsPbBr$_3$ QDs, cesium (b), lead (c), bromine (d) elemental maps.
Figure S6. Time-resolved PL decay of CsPbBr$_3$ QDs.

Figure S7. Time-resolved PL decay for the mixture of CsPbBr$_3$ and Cs$_4$PbBr$_6$ QDs.
Figure S8. Schematic for centrifugation procedure with increased Pb content (the Cs:Pb:Br ratio is shown in the left).

Figure S9. 1H NMR spectrum of CsPbBr$_3$ NCs.
Figure S10. XRD patterns with increased Cs content (the black rhombus represents the peak of Cs$_4$PbBr$_6$).

Figure S11. Schematic for centrifugation procedure with increased Cs content (the Cs:Pb:Br ratios are shown in the left).
Figure S12. XRD patterns with increased Br content (the black rhombus represents the peak of Cs$_4$PbBr$_6$).

Figure S13. Schematic for centrifugation procedure with increased Br content (the Cs:Pb:Br ratio is shown in the left).
Figure S14. TEM image of CsPbBr$_3$ QDs with a Cs:Pb:Br ratio of 1:1:5.

Figure S15. Schematic of the CsPbBr$_3$ (a) and Cs$_4$PbBr$_6$ (b) perovskite lattices.