Supplementary Information

Solvothermal Synthesis of Cesium Lead Halide Nanocrystals with Controllable Dimensions: A Stoichiometry Defined Growth Mechanism

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Experimental Section

Materials: Cesium acetate (CsOAc, 99.998%), lead chloride (PbCl₂, ultradry, 99.999%), lead bromide (PbBr₂, ultradry, 99.999%), lead iodide (PbI₂, ultradry 99.999%), 1-octadecene (ODE, 90%) and oleic acid (OA, 90%) were purchased from Alfa Aesar. N-octylamine (OctAm, 99%) was obtained from Aladdin. Anhydrous hexane was obtained from Sigma-Aldrich. All reagents were used as received without further purification.

Preparation of Cs-oleate (0.15 M) precursor: CsOAc (0.188 g, 0.98 mmol) was loaded in a 20 mL glass vial with ODE (6 mL) and OA (0.5 mL). The mixture was heated to 120 °C until all CsOAc dissolved.

Preparation of PbBr₂ solution (0.025 M): PbBr₂ (0.1 g, 270 µmol) was added into a 20 mL glass vial with 10 mL ODE, 0.5 mL OA and 0.5 mL OctAm in glovebox and heated to 120 °C. After PbBr₂ completely dissolved, the solution was cooled down for further usage.

Preparation of CsPbBr₃ nanocrystals with controllable morphologies: For synthesis of CsPbBr₃ nanocrystals with different morphologies, certain volume of Cs-oleate solution was added. In a typical experiment, as-prepared PbBr₂ stock solution (11 mL) and different volume of Cs-oleate (0.2~0.8 mL) (0.15 M) was added into a Teflon-line autoclave (50 mL) and then placed in a rolling oven. The reaction was kept at 120 °C for 60 minutes.

Preparation of low dimensional CsPbX₃ (X=Cl, Cl/Br, Br/I) nanostructures: For preparation of low dimensional CsPbX₃ (X=Cl, Cl/Br, Br/I) nanostructures, 0.4 mL Cs-oleate (0.15 M) was used. In a typical experiment, PbCl₂ (0.075 g, 0.27 mmol) or PbCl₂/PbBr₂ mixtures and PbBr₂/PbI₂ mixtures with appropriate ratios were loaded into a glass vial (20 mL) with ODE (10 mL), OA (0.5 mL) and OctAm (0.5 mL) in glovebox. The mixture was heated to 120 °C until completely dissolved. Then, 0.4 mL Cs-oleate (0.15 M) was added into PbX₂ stock solution. The mixture was transferred into an autoclave (50 mL) and placed into a rolling oven. The reaction was kept at 120 °C for 60 minutes.

Isolation and purification of nanocrystals: After naturally cooling down to room temperature, products were extracted by centrifugation. 5 mL hexane was added into
the crude solution and then centrifuged at 10000 rpm for 8 minutes to remove the residual reactants. Then, the products were dispersed in 5 mL hexane for further characterization.

**Anion exchange reaction with CsPbBr\textsubscript{3} nanoribbons:** We used CsPbBr\textsubscript{3} nanoribbons as the starting materials to carry out the anion exchange reaction. The anion exchange reaction was conducted in a 10 mL vial. First, PbCl\textsubscript{2} or PbI\textsubscript{2} used as the anion source was dissolved in hexane (5 mL), OA (0.2 mL) and OctAm (0.2 mL) in a vial under inert gas atmosphere. Typically, 0.5 mL CsPbBr\textsubscript{3} nanoribbons solution was dispersed in 5 mL hexane. Then, certain amount of anion source was added into the diluted CsPbBr\textsubscript{3} nanoribbons solution at room temperature to initiate the anion exchange reaction. After several minutes, the products were collected and re-dispersed in hexane for further characterization.

**Characterizations:** The rolling oven (HZ-220) was purchased from Hezongyiqi, Gongyi. UV–vis absorption spectra were recorded in a range of 300-800 nm by using an Evolution 220 spectrophotometer in transmission mode. The PL spectra and PLQY were obtained through a FLUOROMAX-4 spectrofluorometer equipped with a Xenon lamp. PLQY values were collected by using 400 nm as excitation wavelength and a calibrated integrated sphere. The PL lifetime measurements were taken by a HORTB-FM-2015 spectrofluorimeter. The fluorescence digital images of NCs solution under a 365 nm UV light illumination were collected by a Canon EOS 80D camera. Powder X-ray diffraction were performed using a Bruker D8 Advance diffractometer with Cu Kα radiation (λ=1.54056 Å). TEM images were collected by a TECNAI G2 F20 transmission electron microscope with an accelerating voltage 200 kV and a Gatan SC200 CCD camera.
Supplementary Tables and Figures:

**Table S1.** The summary of reaction parameters and optical properties of CsPbBr$_3$ nanocrystals with different morphologies. The amount of Cs precursor was varied while the amount of added PbBr$_2$ precursor was kept at 270 µmol (0.1 g).

<table>
<thead>
<tr>
<th>Cs-oleate precursor (mL)</th>
<th>Cs (µmol)</th>
<th>Morphology</th>
<th>Length/width (nm)</th>
<th>PLQY (%)</th>
<th>Average lifetime (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>30</td>
<td>nanorods</td>
<td>94.7/4.5</td>
<td>18</td>
<td>2.6</td>
</tr>
<tr>
<td>0.4</td>
<td>60</td>
<td>nanoribbons</td>
<td>63.6/10.2</td>
<td>24</td>
<td>4.2</td>
</tr>
<tr>
<td>0.6</td>
<td>90</td>
<td>nanoplatelets</td>
<td>36.9/15.0</td>
<td>31</td>
<td>5.1</td>
</tr>
<tr>
<td>0.8</td>
<td>120</td>
<td>nanocubes</td>
<td>14.2</td>
<td>80</td>
<td>12.4</td>
</tr>
</tbody>
</table>

**Table S2.** The amount of PbBr$_2$ precursor was used to controllably synthesize products. The amount of Cs precursor was kept constant (Cs-oleate=0.4 mL, 60 µmol).

<table>
<thead>
<tr>
<th>PbBr$_2$ precursor (g)</th>
<th>PbBr$_2$ (µmol)</th>
<th>Morphology</th>
<th>Length/width (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.15</td>
<td>406</td>
<td>nanorods</td>
<td>89.0/6.4</td>
</tr>
<tr>
<td>0.069</td>
<td>186</td>
<td>nanocubes</td>
<td>13.5</td>
</tr>
</tbody>
</table>
Fig. S1 TEM images of assembled CsPbBr$_3$ (a) nanoplatelets, (b) nanoribbons and (c) nanorods. All samples were stacked in a face-to-face manner. The model in (a) shows the nanoplatelets were stood titled with the substrate. The models in (b) and (c) show the nanoribbons and nanorods were stood edge-on perpendicular to the substrate.
**Fig. S2** Selected area fast Fourier transform (FFT) pattern of CsPbBr$_3$ nanocubes.
Fig. S3 Selected area fast Fourier transform (FFT) pattern of CsPbBr$_3$ nanoribbons.
Fig. S4 The average lifetimes of CsPbBr$_3$ nanocrystals with different morphologies.
Fig. S5 The enlarged XRD patterns of CsPbBr$_3$ nanoplatelets, nanoribbons and nanorods ($2\theta$=13°-23°).
Fig. S6 EDX spectra of CsPbBr$_3$ (a) nanocubes, (b) nanoplatelets, (c) nanoribbons and (d) nanorods.
Fig. S7 1D CsPbBr$_3$ nanorods obtained by adding 406 µmol of PbBr$_2$ precursor with fixed the amount of Cs precursor. (a-b) TEM images, (c-d) corresponding length and width distribution histograms and (e) UV-Vis and PL emission spectra. CsPbBr$_3$ nanorods emitted bright blue emission. Their lateral side length and width are around 89 nm and width 6.4 nm, respectively.
Fig. S8 3D CsPbBr$_3$ nanocubes obtained by adding 186 μmol of PbBr$_2$ precursor with fixed amount of Cs precursor. (a) TEM image and (b) UV-Vis and PL emission spectra of nanocubes. CsPbBr$_3$ nanocubes show a green emission peak around 517 nm.
Fig. 59 XRD patterns of low dimensional CsPbX$_3$ nanocrystals with different halide (X=Cl, Cl/Br, and Br/I) compositions.
**Fig. S10** UV-Vis spectra of the halide-anion exchanged samples prepared by mixing CsPbBr$_3$ nanoribbons with various concentrations of PbCl$_2$ or PbI$_2$ solution. The absorption spectra of CsPbX$_3$ nanoribbons were varied from 370 nm to 580 nm.
**Fig. S11** TEM images of (a) CsPbCl$_3$ and (b) CsPbI$_3$ nanoribbons obtained from a fast ion-exchange process.