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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 ($PbCl_2$, ultradry, 99.999%), lead bromide ($PbBr_2$, ultradry, 99.999%), lead iodide (PbI_2, ultradry 99.999%), 1-octadecene (ODE, 90%) and oleic acid (OA, 90%) were purchased from Alfa Aesar. N-octlyamine (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 ^{o}C until all CsOAc dissolved.

Preparation of $PbBr_2$ solution (0.025 M): $PbBr_2$ (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 ^{o}C. After $PbBr_2$ completely dissolved, the solution was cooled down for further usage.

Preparation of $CsPbBr_3$ nanocrystals with controllable morphologies: For synthesis of $CsPbBr_3$ nanocrystals with different morphologies, certain volume of Cs-oleate solution was added. In a typical experiment, as-prepared $PbBr_2$ 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 ^{o}C for 60 minutes.

Preparation of low dimensional $CsPbX_3$ (X=Cl, Cl/Br, Br/I) nanostructures: For preparation of low dimensional $CsPbX_3$ (X=Cl, Cl/Br, Br/I) nanostructures, 0.4 mL Cs-oleate (0.15 M) was used. In a typical experiment, $PbCl_2$ (0.075 g, 0.27 mmol) or $PbCl_2$/$PbBr_2$ mixtures and $PbBr_2$/PbI_2 mixtures with appropriate ratios were loaded into a glass vial (20 mL) with OED (10 mL), OA (0.5 mL) and OctAm (0.5 mL) in glovebox. The mixture was heated to 120 ^{o}C until completely dissolved. Then, 0.4 mL Cs-oleate (0.15 M) was added into PbX_2 stock solution. The mixture was transferred into an autoclave (50 mL) and placed into a rolling oven. The reaction was kept at 120 ^{o}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 $CsPbBr_3$ nanoribbons: We used $CsPbBr_3$ nanoribbons as the starting materials to carry out the anion exchange reaction. The anion exchange reaction was conducted in a 10 mL vial. First, $PbCl_2$ or PbI_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 $CsPbBr_3$ nanoribbons solution was dispersed in 5 mL hexane. Then, certain amount of anion source was added into the diluted $CsPbBr_3$ 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).

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

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).

$PbBr_2$ precursor (g)	$PbBr_2$ (µmol)	Morphology	Length/width (nm)
0.15	406	nanorods	89.0/6.4
0.069	186	nanocubes	13.5

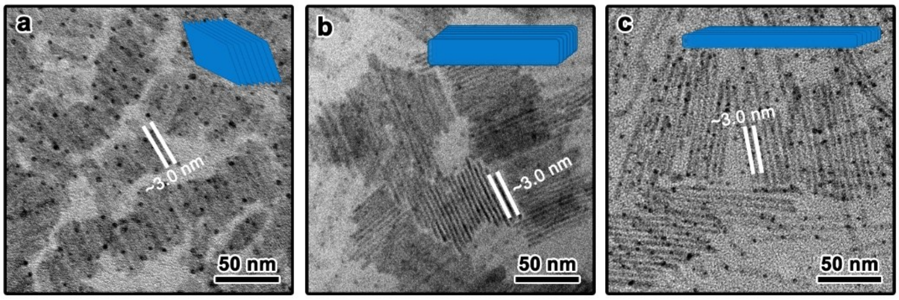


Fig. S1 TEM images of assembled $CsPbBr_3$ (a) nanoplatelets, (b) nanoribbons and (c) nanorods. All samples were stacked in a face-to-face manner. The model in (a) shows the nanoplatelets were stood titled with the substrate. The models in (b) and (c) show the nanoribbons and nanorods were stood edge-on perpendicular to the substrate.

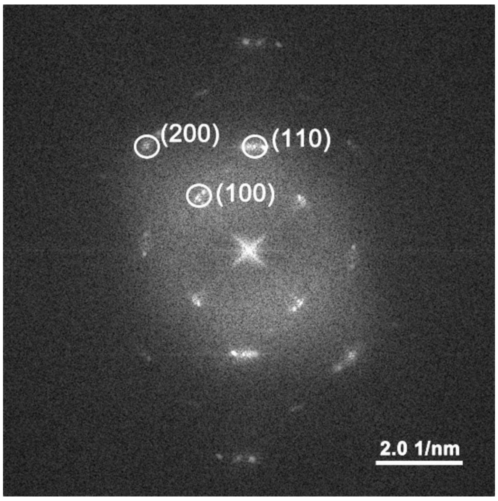


Fig. S2 Selected area fast Fourier transform (FFT) pattern of $CsPbBr_3$ nanocubes.

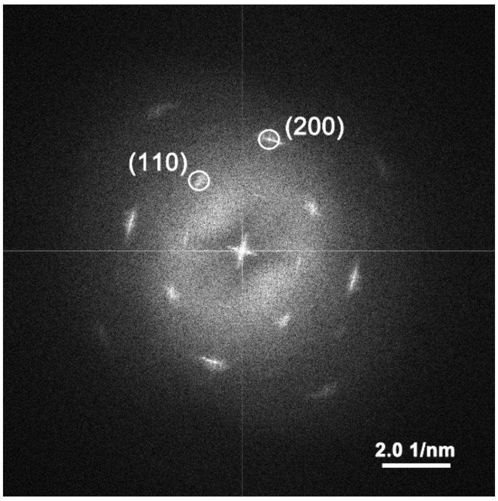


Fig. S3 Selected area fast Fourier transform (FFT) pattern of $CsPbBr_3$ nanoribbons.

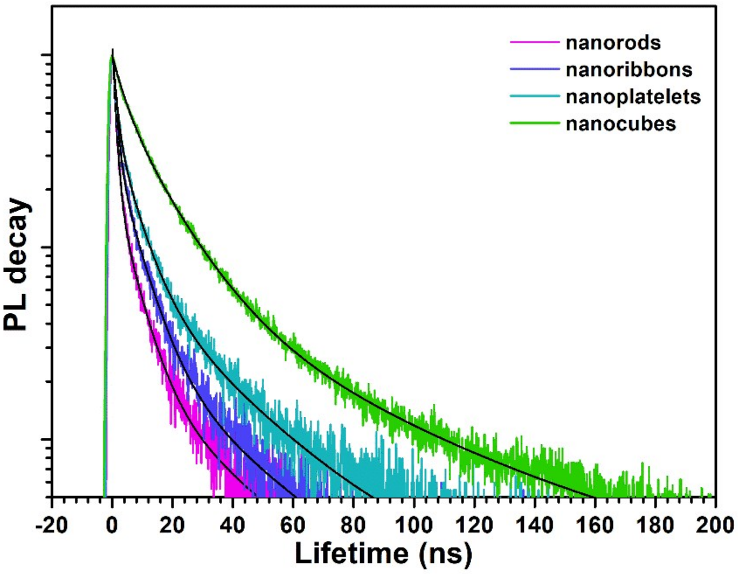


Fig. S4 The average lifetimes of $CsPbBr_3$ nanocrystals with different morphologies.

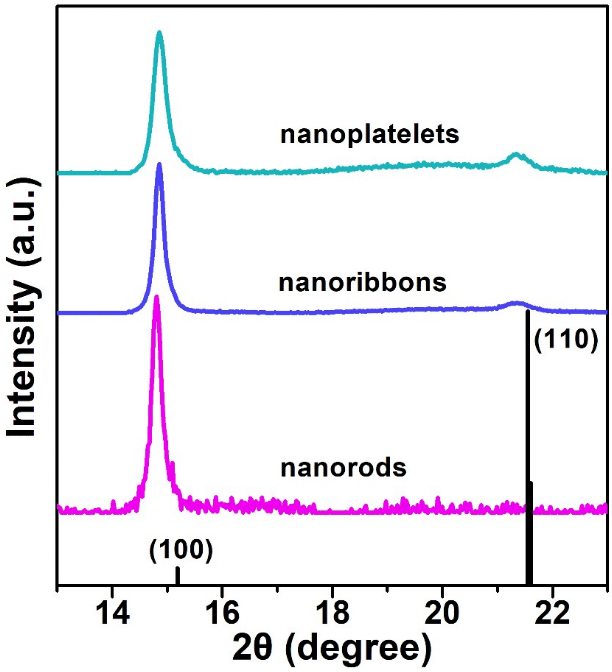
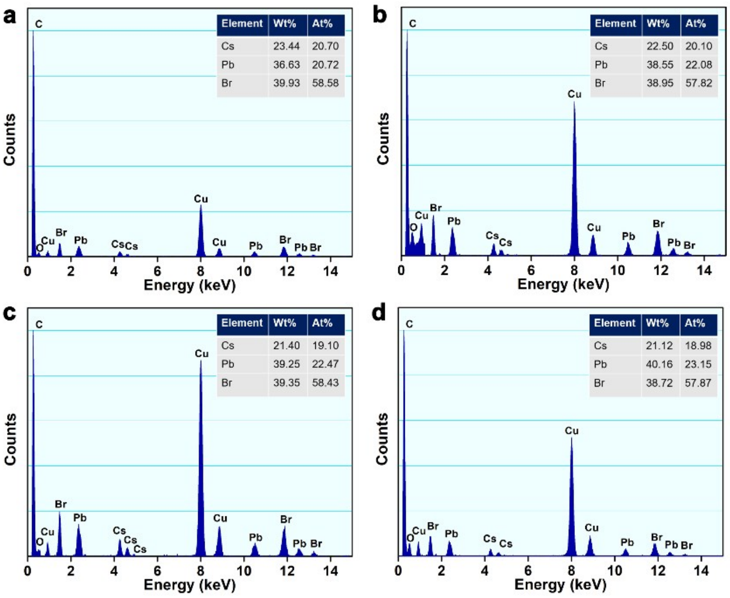


Fig. S5 The enlarged XRD patterns of $CsPbBr_3$ nanoplatelets, nanoribbons and nanorods ($2\theta=13^o-23^o$).



a

Element	Wt%	At%
Cs	23.44	20.70
Pb	36.63	20.72
Br	39.93	58.58

b

Element	Wt%	At%
Cs	22.50	20.10
Pb	38.55	22.08
Br	38.95	57.82

c

Element	Wt%	At%
Cs	21.40	19.10
Pb	39.25	22.47
Br	39.35	58.43

d

Element	Wt%	At%
Cs	21.12	18.98
Pb	40.16	23.15
Br	38.72	57.87

Fig. S6 EDX spectra of $CsPbBr_3$ (a) nanocubes, (b) nanoplatelets, (c) nanoribbons and (d) nanorods.

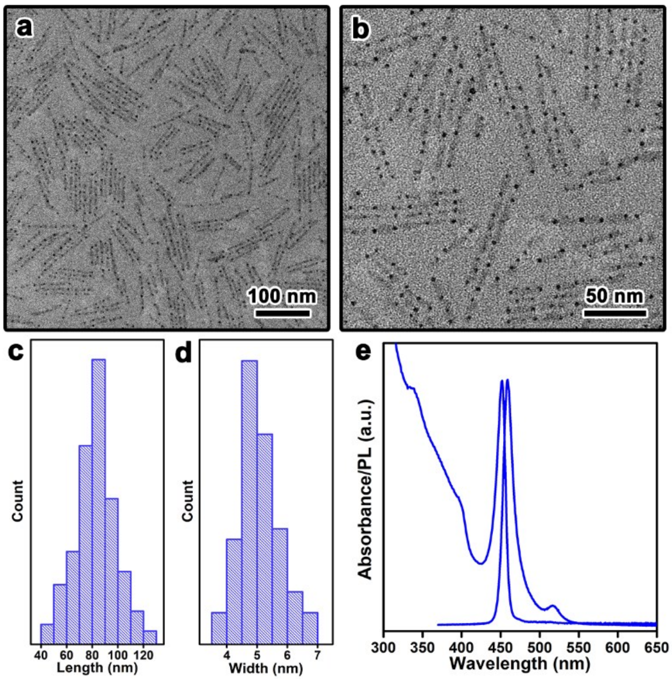


Fig. S7 1D $CsPbBr_3$ nanorods obtained by adding 406 µmol of $PbBr_2$ precursor with fixed the amount of Cs precursor. (a-b) TEM images, (c-d) corresponding length and width distribution histograms and (e) UV-Vis and PL emission spectra. $CsPbBr_3$ nanorods emitted bright blue emission. Their lateral side length and width are around 89 nm and width 6.4 nm, respectively.

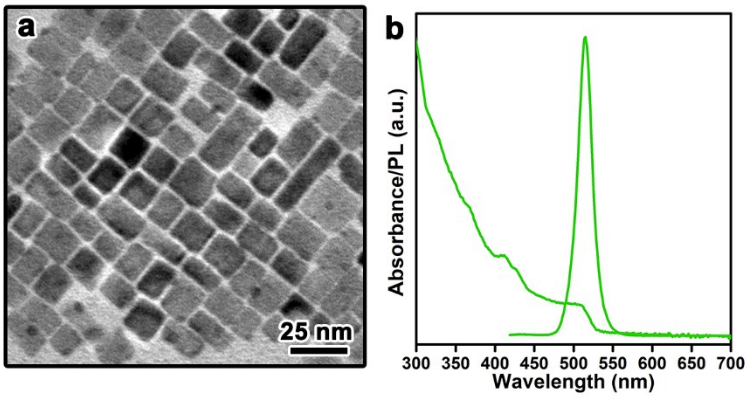


Fig. S8 3D $CsPbBr_3$ nanocubes obtained by adding 186 μmol of $PbBr_2$ precursor with fixed amount of Cs precursor. (a) TEM image and (b) UV-Vis and PL emission spectra of nanocubes. $CsPbBr_3$ nanocubes show a green emission peak around 517 nm.

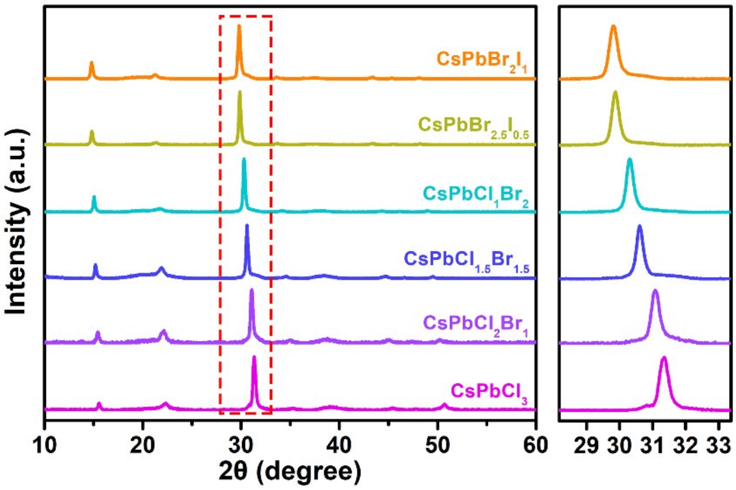


Fig. S9 XRD patterns of low dimensional CsPbX$_3$ nanocrystals with different halide (X=Cl, Cl/Br, and Br/I) compositions.

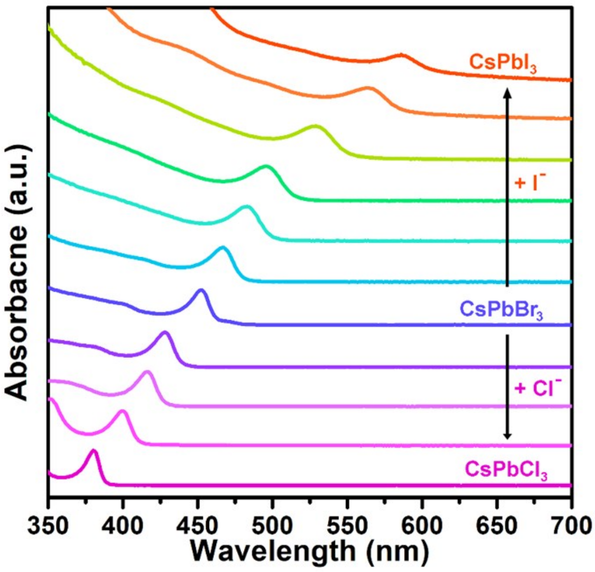


Fig. S10 UV-Vis spectra of the halide-anion exchanged samples prepared by mixing CsPbBr$_3$ nanoribbons with various concentrations of PbCl$_2$ or PbI$_2$ solution. The absorption spectra of CsPbX$_3$ nanoribbons were varied from 370 nm to 580 nm.

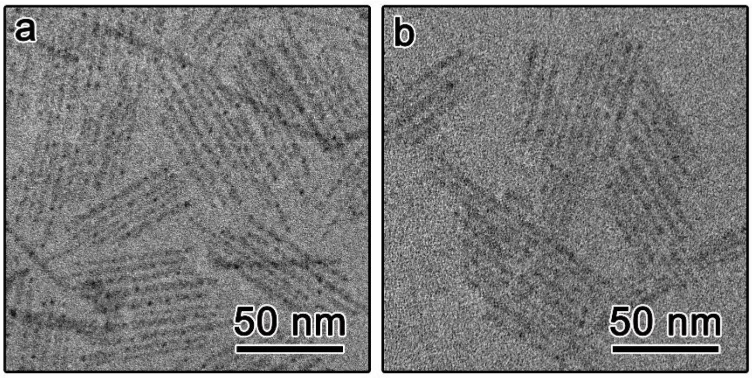


Fig. S11 TEM images of (a) $CsPbCl_3$ and (b) $CsPbI_3$ nanoribbons obtained from a fast ion-exchange process.