Supporting information

Shape and Phase Evolution from $CsPbBr_3$ Perovskite Nanocubes to Tetragonal $CsPb_2Br_5$ Nanosheets with Indirect Bandgap

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Experimental Section

1.Materials

Organic reagents including oleic acid (HOA, 90 %), n-octylamine (n-OCA, 99 %), tri-octylamine (n-Tri-OCA, 95%), Octadecylene (ODE,≥90%) were purchased from Aladdin. Toluene was purchased from Sinpharm Chemical Rwagents Co. Ltd. Inorganic compounds including lead bromide ($PbBr_2$,99%), Cesium carbonate (Cs_2CO_3, 99.9%) were purchased from Aladdin. All regents were used directly without further purification.

2.Preparation of Cs-oleate (Cs-OA)

In a typical experiment, Cs_2CO_3 (0.8 g), HOA (2.5 ml) and ODE (30 ml) were added into a 100 ml 3-neck flask, degassed at room temperature for 30min and then dried for 1h at 120 ºC under Ar until all Cs_2CO_3 reacted with HOA.

3. Synthesis method

ODE (8.68 ml), n-Tri-OCA (2.64 ml), HOA (1 ml) and $PbBr_2$ (0.138 g) were added into a 100 ml 3-neck flask. The mixture was degassed and heated to 120 ºC for 1h. n-OCA (0.25 ml) and HOA (0.4 ml) were added into the flask and then the mixture was heated to 160 ºC under Ar until all $PbBr_2$ dissolved. Cs-OA (0.8 ml) was injected into the flask under 160 ºC. The reaction was terminated at the certain time of 5 s, 10 min, 30 min, 1 h, 2 h, 3 h, 6 h, respectively, and the crude solution was quenched by toluene.

4.Isolation and purification the nanocrystals

After quenching, the crude solutionwas cooled down to room temperature and centrifugated at 4000 rpm for 10min to obtain precipitation. Then the precipitation was dispersed into toluene for TEM, optical spectra measurements. And for XRD and AFM measurements, the sample needed to wash more 1 or 2 times with toluene.

5. Density functional theory (DFT) calculations

The calculations of electronic band structure and the free energy were performed using density functional theory with the projector-augmented wave method.[1] The generalized gradient approximation (GGA) function of Perdew and Wang (PW91) was adopted to treat the exchange and correlation potentials in all calculations.[2] The effective core potential was used for the electron-ion interactions, and the cut-off energy was set to 500 eV. The Brillouin zone sampling k-point set-mesh parameters were 5×5×5.

6. Characterization

All measurements were performed at room temperature. The TEM and HRTEM images were obtained on a JEM-2100 field emission source transmission electron microscope operating at 200 kV. X-ray diffraction patterns were measured by a Rigaku D/MaxrB diffraction using Cu Kα radiation with a wavelength of 0.1540 nm. UV-vis absorbance and fluorescence spectra were acquired by a Shimadzu UV-2550 ultraviolet-visible (UV-vis) spectrophotometer and Hitachi F-4500 fluorescenece spectrophotometer. Tapping-mode atomic AFM images were obtained on a Bruker dimension fastscan platform.

Supporting Figures

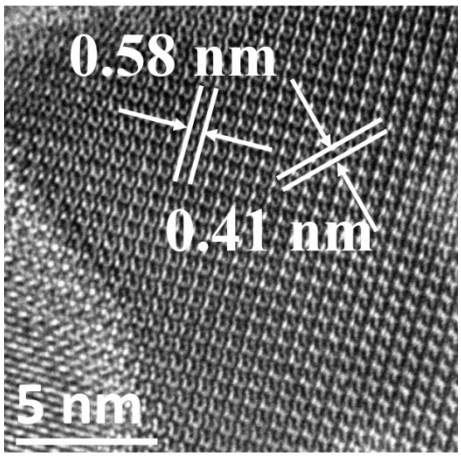

Fig.S1 The HRTEM image of orthorhombic $CsPbBr_3$nanosheetsobtained at 1h. The 0.58 nm and 0.41 nm could be indexed to the (110) and (020)/(200) crystal planes of orthorhombic $CsPbBr_3$.

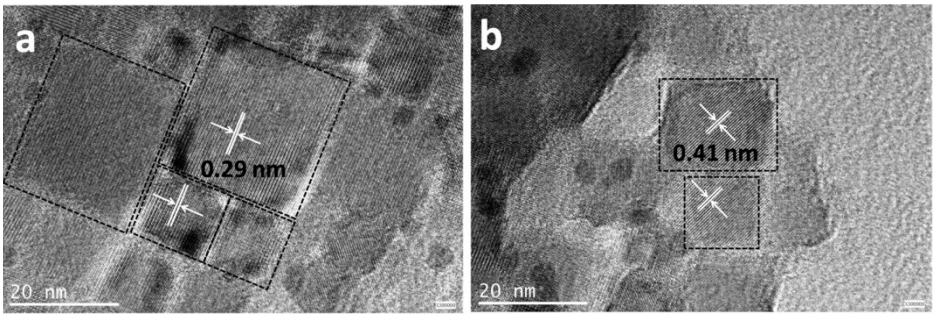

Fig. S2 Typical HRTEM images showing the $CsPbBr_3$ nanocubes coalescence via OA mechanism at 10 min. The arrows show the traces of coalescence. The 0.29 nm and 0.41 nm could be indexed to (220) and (020)/(200) crystal planes of orthorhombic $CsPbBr_3$.

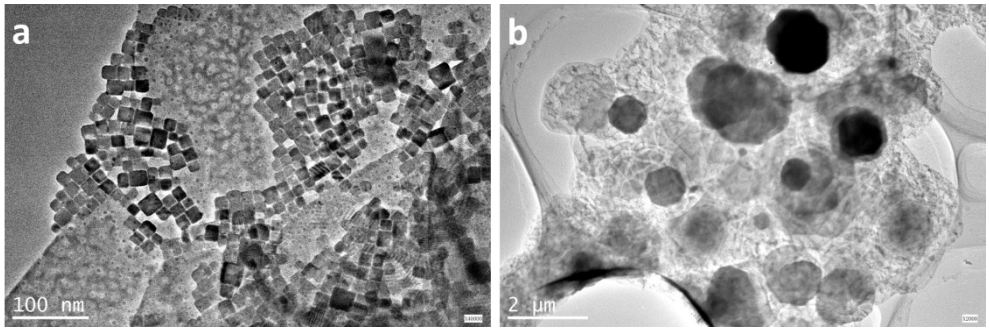

Fig. S3 The TEM images of the sample obtained at 30 min with different magnification.

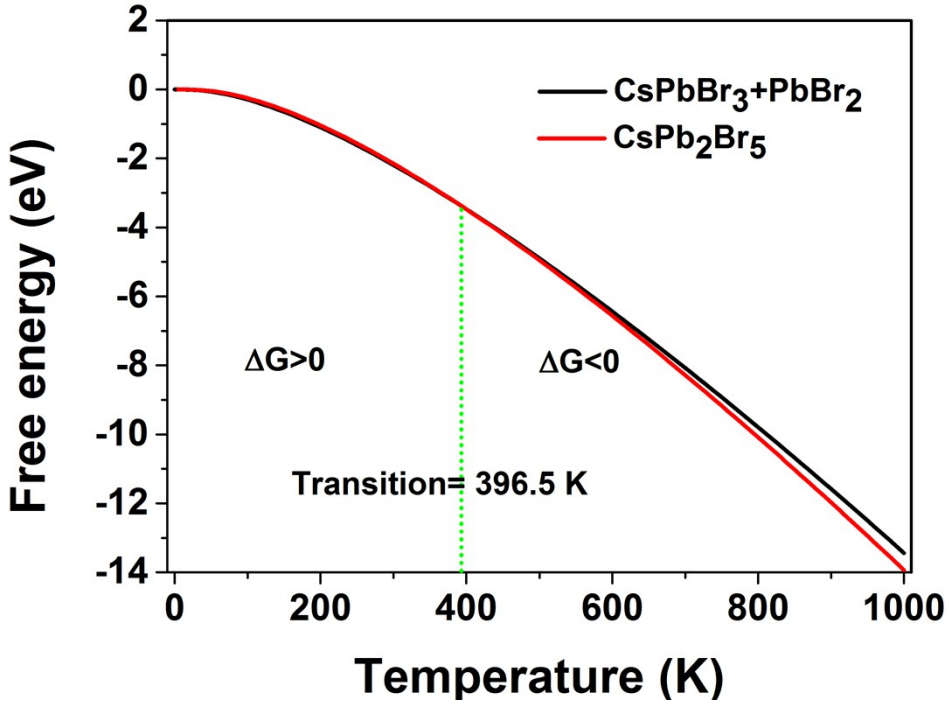

Fig. S4 The free energy of $CsPbBr_3$ +$PbBr_2$, $CsPb_2Br_5$, as well as active temperature.

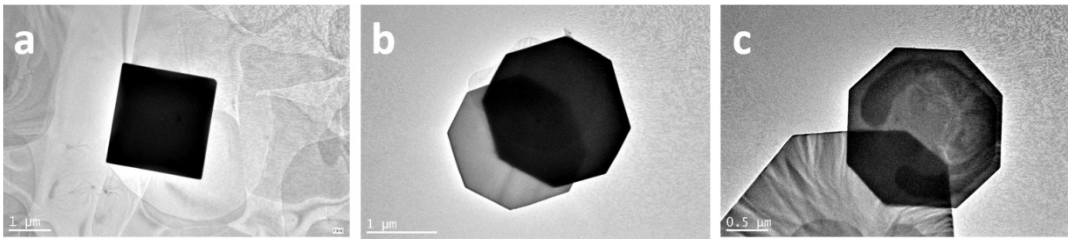

Fig. S5 The typical TEM images of $CsPb_2Br_5$nanosheets.

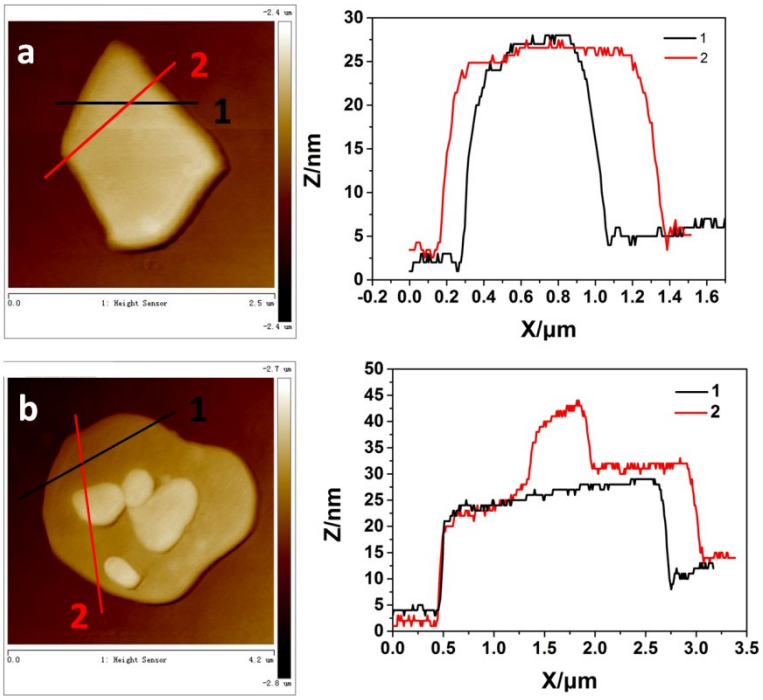

Fig. S6 AFM images of $CsPb_2Br_5$nanosheets obtained at 2 h.

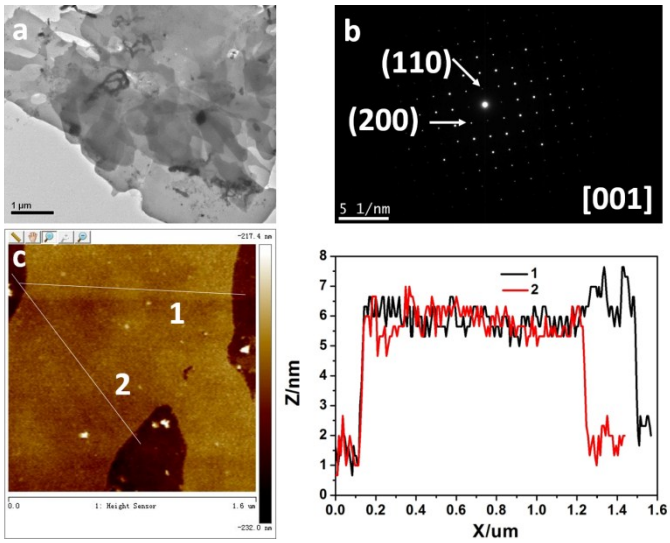

Fig. S7 The (a) TEM, (b) SAED and (c) AFM images of ultrathin $CsPb_2Br_5$nanosheets.

References

1 P. E. Blöchl, *Phys Rev B*, 1994, **50**, 17953.

2 J. P. Perdew and W. Yue, *Phys Rev B*, 1986, **33**, 8800.