Supporting Information

Single crystal growth of $CsPb_2Br_5$

0.3 mmol of CsBr powder (0.06 g, Aladdin, 99%) was dissolved in 2 mL deionized HBr (47% AY, Aladdin) to obtain Cs-solution. 0.6 mmol of $PbBr_2$ (0. 22 g, Aladdin, 99%) powder was dissolved in 3 mL HBr (47% AY, Aladdin) to obtain Pb-solution. Keeping the two solutions heated at 90 ℃, then adding Cs-Solution into Pb-solution by dropwise under vigorous stirring. Finally, clear solution was obtained. Then slowly cooling the solution from 90 ℃ to room temperature. If keeping a slow cooling rate about 5 ℃/h, large-area transparent flake crystals up to 5×5 mm^2 can be obtained only after 2.5 h, the photos of the crystals during the cooling process can be clearly seen in Fig. S1. If keeping a faster cooling rate about > 10 ℃/h, namely natural cooling, some small-area colorful crystals can be obtained in less than 0.5 h. The video of the crystal growth during the cooling process is also given. Optical microscope photos of the crystals on sapphire (Fig. 1b) were taken by an optical microscope (OM; Nikon). The thicknesses of the crystals are measured by Atomic Force Microscope (Dimension Edge; Bruker).

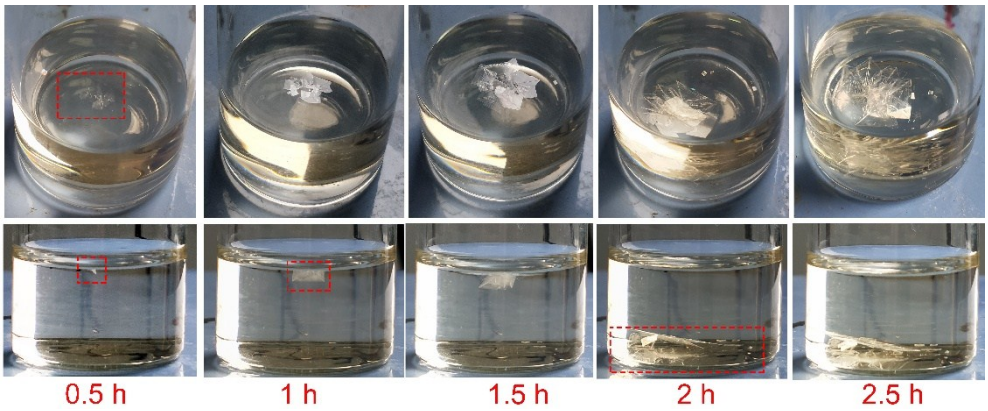

Fig. S1 The growth of large area bulk $CsPb_2Br_5$ flake single crystal during the solution cooling process. The small crystal flakes are firstly formed by floating on the solution surface. With solution temperature decreasing, the crystal flakes grown larger and larger and finally dropped to the bottom of the bottle owing to its gravity.

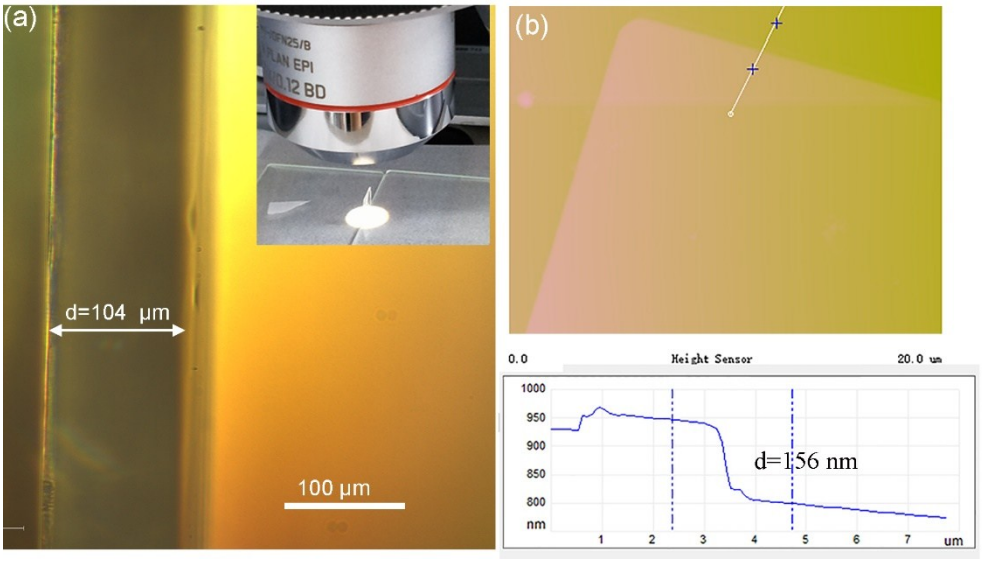

Fig. S2 (a) The cross-sectional photo of the bulk larger-area $CsPb_2Br_5$ flake crystals, indicating a thickness of 104 μm. The inset shows the measurement photo. (b) The

thickness of the bulk purple $CsPb_2Br_5$ single crystal measured by AFM.

Structure and composition analysis

The single crystal data were obtained using an Agilent Supernova diffractometer with using Mo Kα beam with λ = 0.71073 Å at 150 K cooled by liquid nitrogen. Cell refinement and data integration were operated using CrysAlis Pro Software by Agilent Technologies Ltd. Single crystal structure of $CsPb_2Br_5$ was resolved by Direct methods and refined using SHELXL 2016 software package.

Table S1 Crystallographic Data for a $CsPb_2Br_5$ single crystal

Chemical formula	$CsPb_2Br_5$
Formula Mass	1893.68
Crystal system	Tetragonal
Lattice parameters	$a = b$ =8.45060(10) Å c=15.0669(5) Å $\alpha=\beta=\gamma$=90°
Unit cell volume/Å^3	1075.97(4)
Calculated density/Mg/m^3	5.845
Temperature/K	150(2)
Space group	*I*4/*mcm*(140)
No. of formula units per unit cell, Z	2
Radiation type	Mo Kα
Absorption coefficient, μ/mm^{-1}	53.080
No. of reflections measured	3967
No. of independent reflections	438
R_{int}	0.0803
Final R_1 values ($I > 2\sigma(I)$)	0.0544
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1625
Final $wR(F^2)$ values (all data)	0.1646
Goodness of fit on F^2	1.080
Weight scheme for the refinement	Weight = 1 / [sigma^2(Fo^2) + (0.1300 * P)^2 + 9.00 * P] where P = (Max (Fo^2, 0) + 2 * Fc^2) / 3

Table S2 A list of near neighbors of the various atoms in $CsPb_2Br_5$.

	Neighbors	Distance, Å
Pb	$2Br_{II}$	2.88
	$2Br_I$	3.14
	$4Br_{II}$	3.36
	1Pb	4.04
Br_I at (000)	4Pb	3.14
	2Cs	3.77
	$8Br_{II}$	3.75
Br_{II} at $(x, \frac{1}{2}+x, z)$	1Pb	2.88
	2Pb	3.36
	2Cs	3.68
	$2Br_I$	3.75
	$1Br_{II}$	4.53
Cs	$2Br_I$	3.77
	$8Br_{II}$	3.68

Powder X-ray diffraction (PXRD) patterns of the synthesized powder and single crystals were obtained a Bruker D8 advance powder diffractometer (Cu-Kα1 radiation; λ = 154.05 pm) at room temperature.

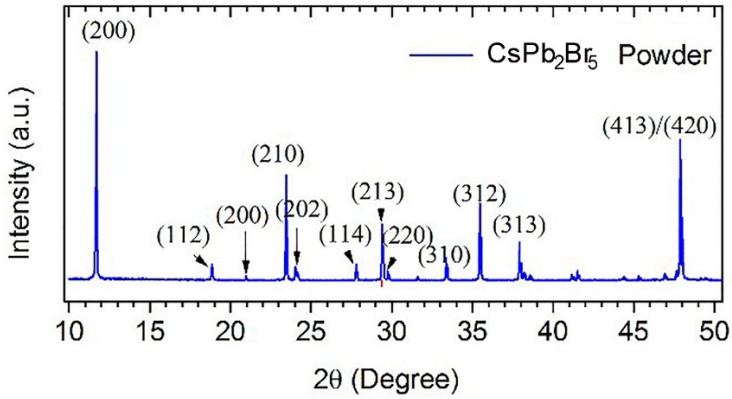

Fig. S3 The indexed PXRD pattern of the grown $CsPb_2Br_5$ crystal.

The elemental composition of the grown $CsPb_2Br_5$ crystal was analyzed by the Energy Dispersive Spectrometer (with 20 kV operation voltage) of Focused ion beam etching

system (Auriga, Zeiss)

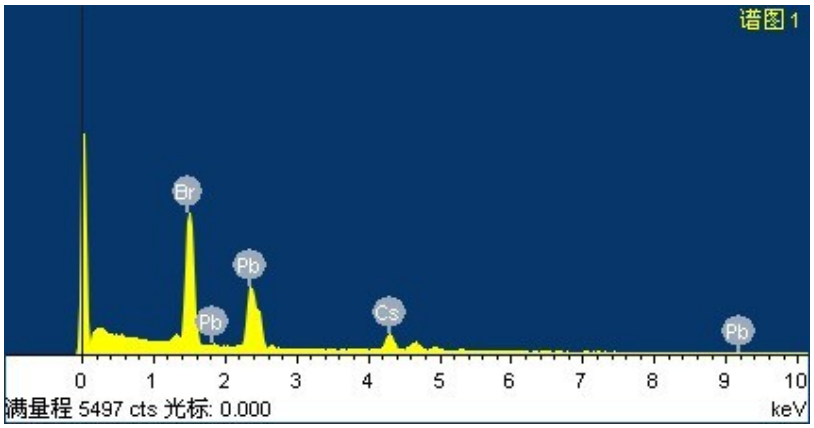

Fig. S4 The EDS spectrum of $CsPb_2Br_5$ SC.

Table S3 Elemental ratio of $CsPb_2Br_5$ SC obtained from the EDS analysis

Element	Weight ratio	Atomic ratio
Br L	43.13	63.22
Cs L	14.62	12.89
Pb M	42.25	23.89
Sum	100.00	

Optical properties characterization

Transmittance spectrum of the transparent bulk $CsPb_2Br_5$ crystal was measured using Shimadzu 2600 UV-Visible spectrophotometer at room temperature.

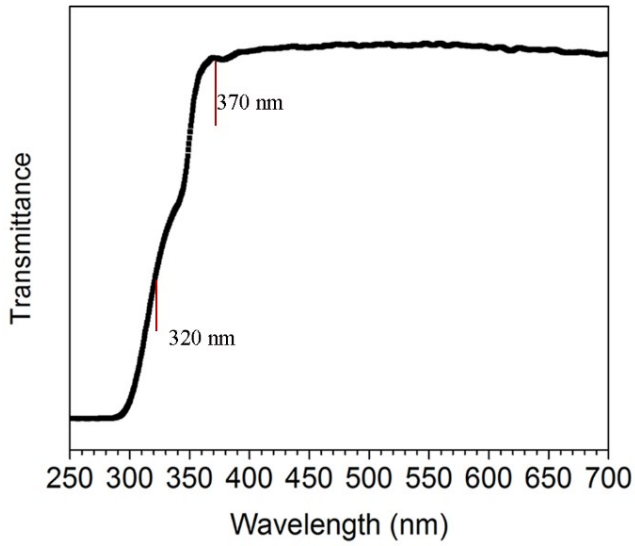

Fig. S5 The transmittance of the bulk transparent $CsPb_2Br_5$ flake SC.

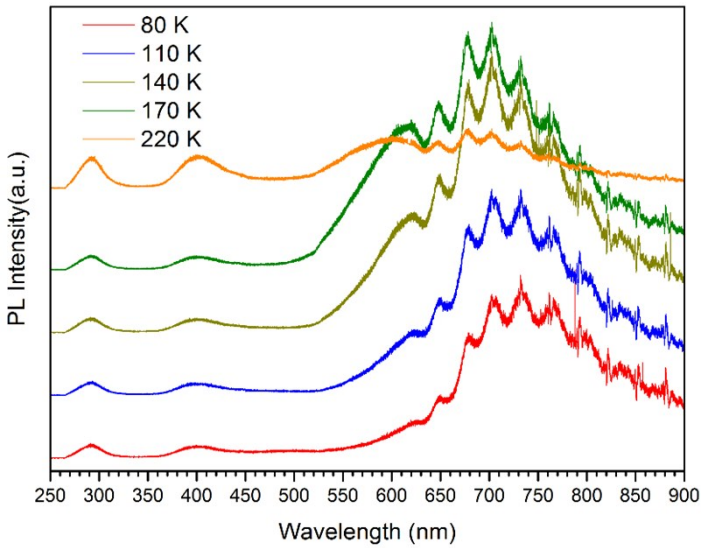

Fig. S6 PL spectra of $CsPb_2Br_5$ SC measured with using 261 nm laser as excitation at 80 -220 K.

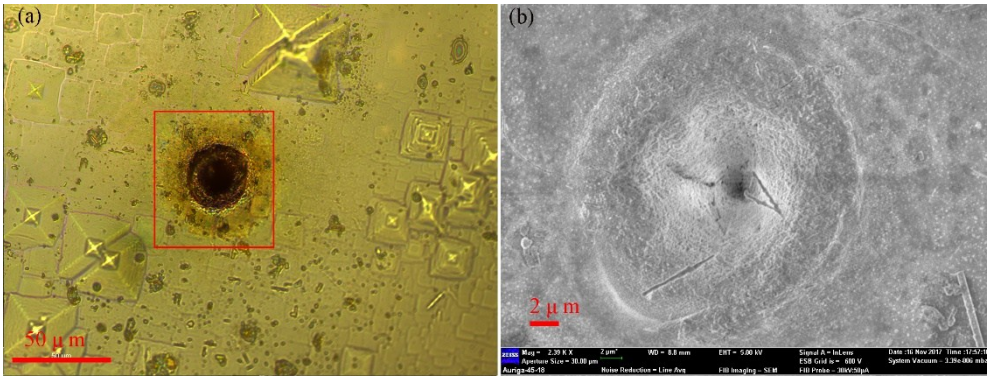

Fig. S7 The (a) optical microscopy photo and (b) scanning electronic microscopy image of $CsPb_2Br_5$ SC after 325 nm laser irradiation, and the red box denote the "corrosion pit" caused by the laser irradiation.

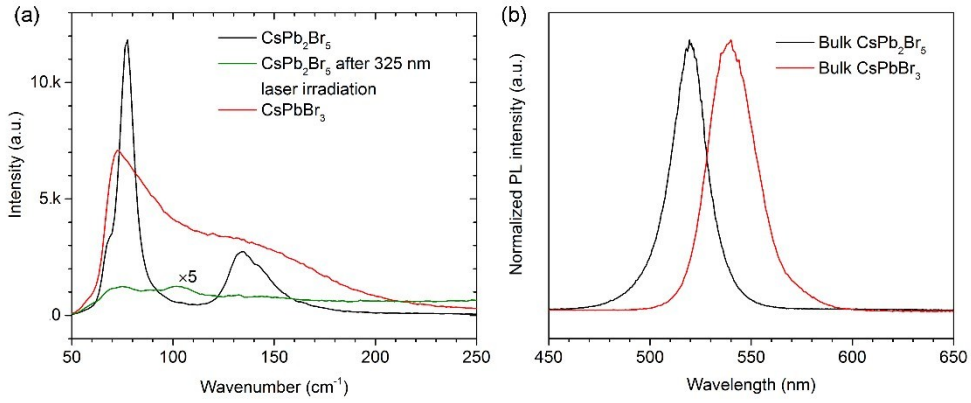

Fig. S8 (a) The room temperature Raman scattering spectra of $CsPb_2Br_5$ SC, $CsPb_2Br_5$ SC after 325 nm laser irradiation, and $CsPbBr_3$ SC measured using 633 nm laser as excitation. (b) Normalized room temperature PL spectrum of $CsPbBr_3$ SC and $CsPb_2Br_5$ SC with using 325 nm laser as excitation light.

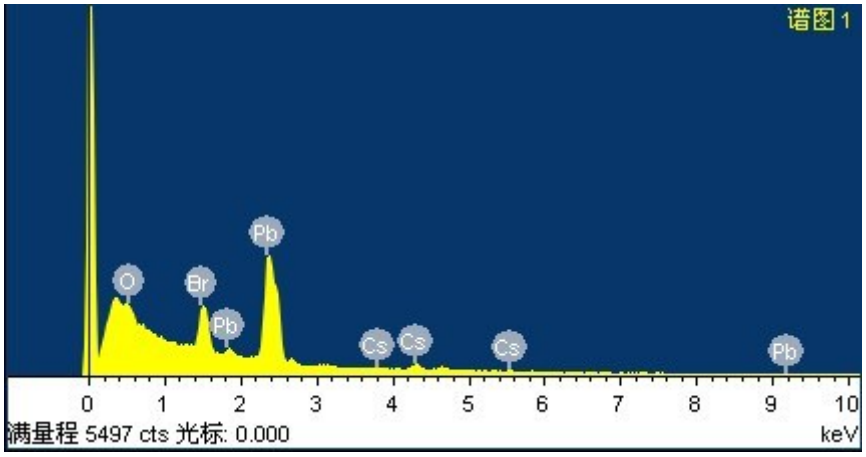

Fig. S9 The EDS spectrum of "hole" on the $CsPb_2Br_5$ SC after 325 nm laser irradiation.

Table S4 Elemental ratio of the "hole" on the $CsPb_2Br_5$ SC produced by 325 nm laser irradiation obtained from the EDS analysis

Element	Weight ratio	Atomic ratio
Br L	17.86	19.01
Cs L	6.84	4.37
Pb M	65.98	27.08
O	9.32	49.54

Sum	100.00

Energy band structure calculation

First-principle calculations have been performed for $CsPb_2Br_5$ using projected augmented plane-wave (PAW) method as implemented in the VASP code package. Exchange and correlation energy was treated under the generalized-gradient-approximation (GGA) including the Perdew-Burke-Ehrenkof (PBE) functional. We used plane-wave energy cutoff of 500eV. A $5 \times 5 \times 5$ k-mesh was used during structure relaxation for the unit cell until the energy difference was converged within 10^{-5}eV, whit the Hellman-Feynman force acting on the atoms were less than 0.1eV/Å. Then the electronic structure and optical properties were calculated.