Electronic Supplementary Information

Low-temperature architecture of cubic-phase $CsPbBr_3$ single crystal for ultrasensitive weak-light photodetector

Xiangfeng Wei,[a,‡] *Han Liu*,[a,‡] *Zhixiang Zhang*,[b] *Wenchao Xu*,[a] *Wenjun Huang*,[a] *Lin-Bao Luo*,[b,*] *and Jiehua Liu*[a,c,*]

[a] Future Energy Laboratory, School of Materials Science and Engineering, Hefei University of Technology, Hefei, 230009, China

[b] School of Electronic Science and Applied Physics, Hefei University of Technology, Hefei, 230009, China

[c] Key Laboratory of Advanced Functional Materials and Devices of Anhui Province, Hefei, 230009, China

AUTHOR INFORMATION

Corresponding Author

* liujh@hfut.edu.cn, luolb@hfut.edu.cn

[‡]X. Wei and H. Liu contributed equally.

Experimental Section

1. Preparation of precursor solution

The saturated solubility of CsBr or $PbBr_2$ was firstly investigated in the DMSO solution with excess CsBr or $PbBr_2$ by increasing temperature from 40 to 60 °C. The saturated solubility of CsBr or $PbBr_2$ in H_2O and DMSO mixed solution was measured by drying 0.5 g saturated solution at 100 °C for 0.5 hours. The saturated solubility was also investigated in mixed H_2O and DMSO solution with different mass ratios (0 to 50% of H_2O/(H_2O + DMSO)). Saturation solubility of CsBr and $PbBr_2$ with an equal molar quantity was confirmed as shown in Table S1. The solution was placed at a constant temperature of 60 °C for 6 h and then filtered with a 0.22 μm nylon filter. The filtered solution was then placed in a sample bottle and sealed for future use.

2. $CsPbBr_3$ single crystal growth

The anti-solvent and co-solvent method was used to realize the growth of single crystal at low temperature. First of all, the above DMSO/H_2O solution has a 1:1 ratio of CsBr/$PbBr_2$ was titrated by acetonitrile as the anti-solvent to saturation. The proportion of the solution and acetonitrile is 1: 0.09 to make sure that the solution is closed to saturation. The solution was added to a small glass bottle. Then it was put into a big bottle with acetonitrile. After sealed, the bottles were put into an oven at 35 °C and then heating with a rate of 0.3 °C/h to 46 °C. The obtained orange single crystal was dried for physical characterization and testing.

3. Fabrication of photodetector

Au/$CsPbBr_3$/Au photodetectors were fabricated on (100) facet of cubic $CsPbBr_3$ single crystals. Au electrodes with a width of 14 μm were evaporated on the crystal surface when using a mask plate made of Ag micro-wire with a diameter of 10 μm by thermal evaporation.

4. Characterizations

X-ray diffraction (XRD) patterns were measured with X' Pert PRO MPD X-ray diffractometer using Cu K_α radiation at 40 kV and 40 mA. Here, both powder and single crystals XRD were characterized. A field emission scanning electron

microscope (SEM, HITACHI UHR FE-SEM SU8020) was used to obtain SEM images of the concave surface. The steady-state photoluminescence measurements were acquired with an Edinburgh FLS920 fluorescence spectrometer at an excitation wavelength of 490 nm. UV-Vis spectrum was measured on Agilent. UV-Vis spectrophotometer (CARY 5000) with an integrating sphere over the spectral range of 300-800 nm.

Time-resolved photoluminescence (TRPL) spectra were obtained by using the time-correlated single-photon counting technique (TimeHarp 260), and the excitation was provided by a picosecond diode laser (PicoQuant) at the wavelength of 510 nm. The photoluminescence intensity decay curve was fitted with a double exponential decay equation as follows:

$$I(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) \quad (1)$$

In this function, I is the decaying intensity, A_1 and A_2 are the decay amplitude and τ_1 and τ_2 are the fitted decay lifetimes of which the small constant τ_1 is ascribed to recombination due to surface traps and the large time constant τ_2 to the bulk traps. The average lifetime was determined as follows:

$$\tau_{av} = \frac{A_1{\tau_1}^2 + A_2{\tau_2}^2}{A_1\tau_1 + A_2\tau_2} \quad (2)$$

The optoelectronic characterization of the single-crystal photodetectors was carried out at room temperature with a semiconductor characterization system (Keithley 4200-SCS), using a laser diode (520 nm) as the illumination source. The power intensity of the incident light was calibrated by a power meter (Thorlabs GmbH., PM100D). To further understand the photoelectric performance of the device, we determined the responsivity (R), external quantum efficiency (EQE), and detectivity (D*) which are three key parameters for photodetectors. Responsivity represents the ratio of photon-excited current to irradiation flux. EQEs can be obtained from responsivity by changing the ratio of current/incident light power to electron quantity/photon quantity to evaluate the photocurrent conversion ability of our devices on different lattice planes. D* is the parameter that characterizes the sensitivity of the detector. The equations are shown below:

$$R = \frac{I_{pc} - I_{dark}}{P \times S} \quad (3)$$

$$EQE = R \times \frac{hc}{e\lambda} \quad (4)$$

$$D^* = R \times \sqrt{\frac{S}{2q \times I_{dark}}} \quad (5)$$

Where I_{pc} is the photocurrent under illumination and I_{dark} is dark current, P is the irradiance power density, and S is the effective illuminated area. Then c stands for the speed of light, e is the elementary charge, and λ is the wavelength of the light source.

Table S1. The equal molar solubility of $CsBr/PbBr_3$ with different H_2O and DMSO at different temperature

Temperature (°C)	**DMSO (wt%)**	**H_2O (wt%)**	**Equal molar solubility of $CsBr/PbBr_3$ (mol/100g)**
40	61.8	38.2	**0.056**
45	**61.9**	**38.1**	**0.060**
50	63.2	36.8	**0.065**
60	72.8	27.2	**0.111**

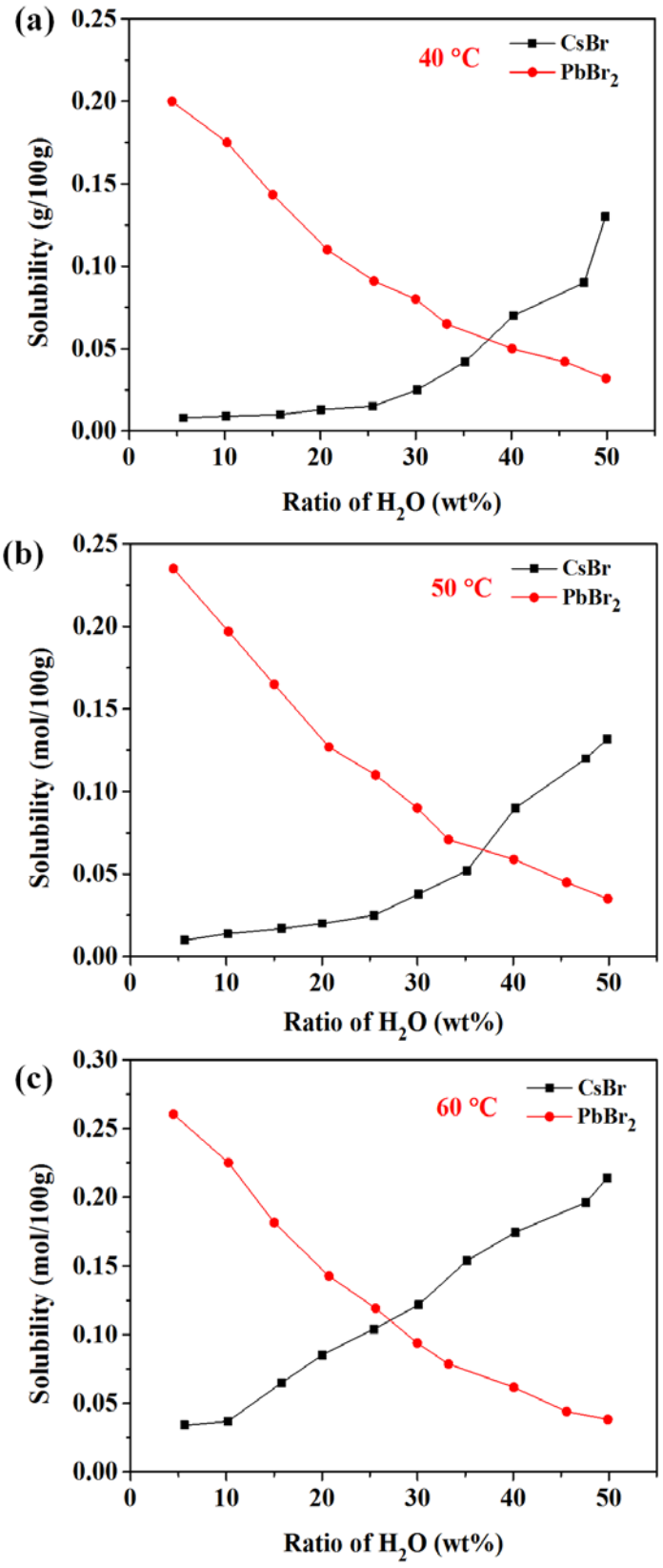

Figure S1. The saturation solubility curves of CsBr and $PbBr_2$ in DMSO-H_2O solution at 40, 50, and 60 °C.

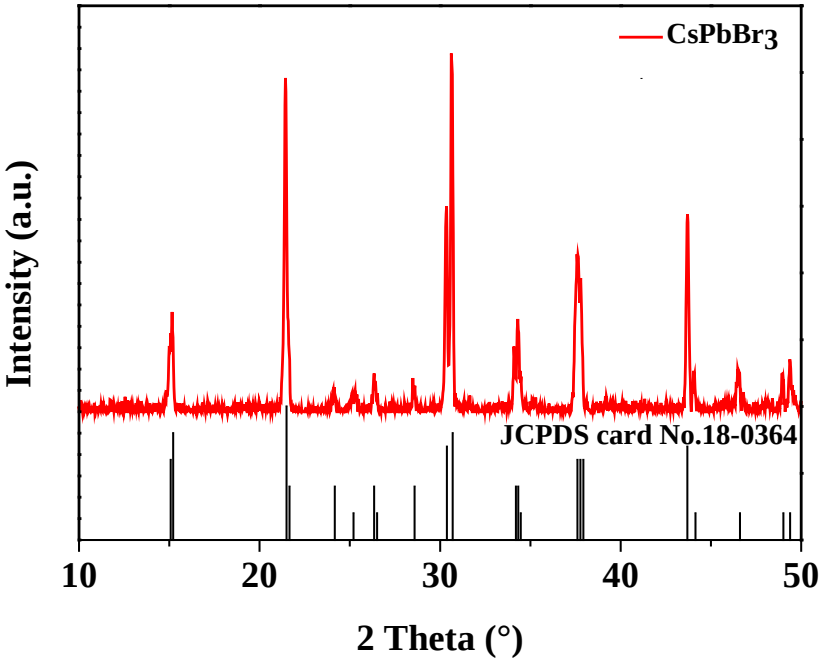

Figure S2. Powder XRD pattern of $CsPbBr_3$.

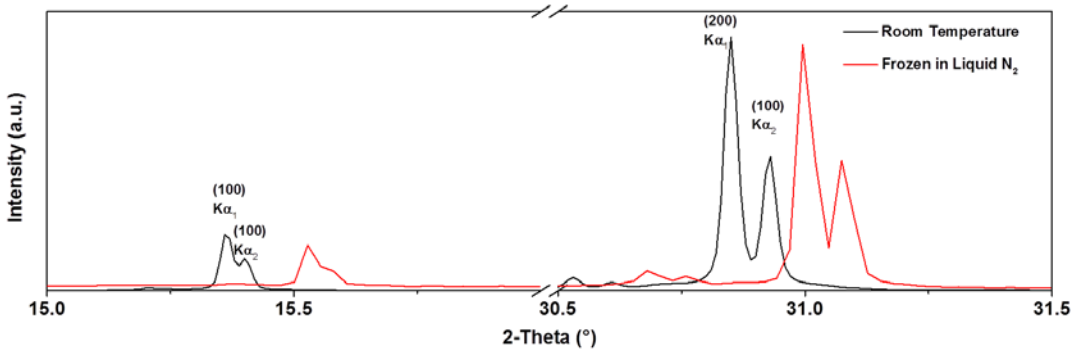

Figure S3. XRD patterns of $CsPbBr_3$ single crystals in high-precision scanning at room temperature and frozen in liquid N_2. The frozen single crystal was obtained after first put in liquid N_2 for 3 hours and stored at room temperature for 5 hours.

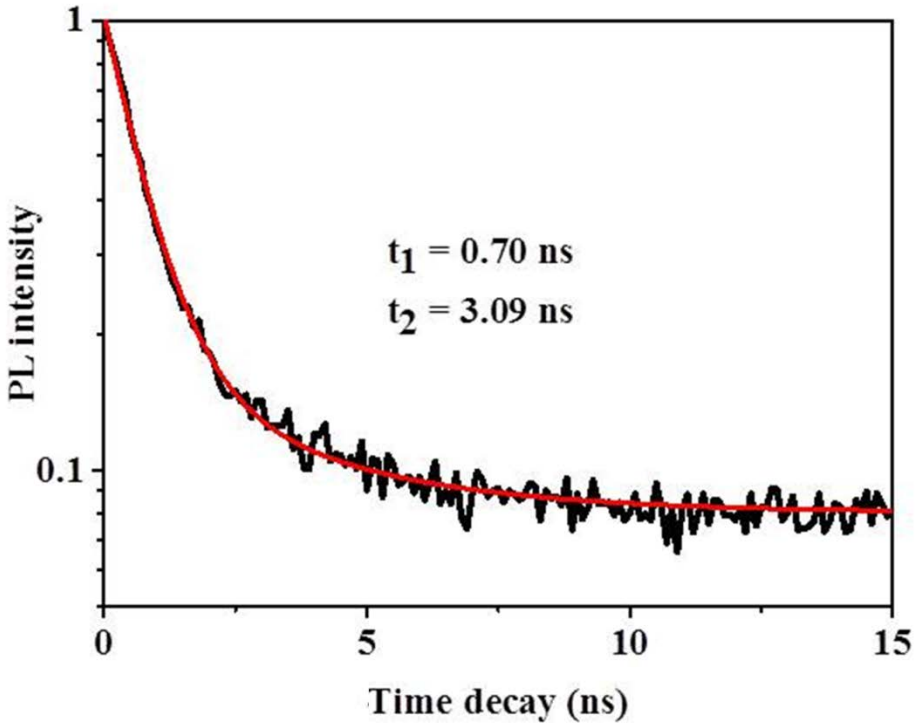

Figure S4. Time-resolved steady-state photoluminescence of cubic-phase $CsPbBr_3$ single crystal.

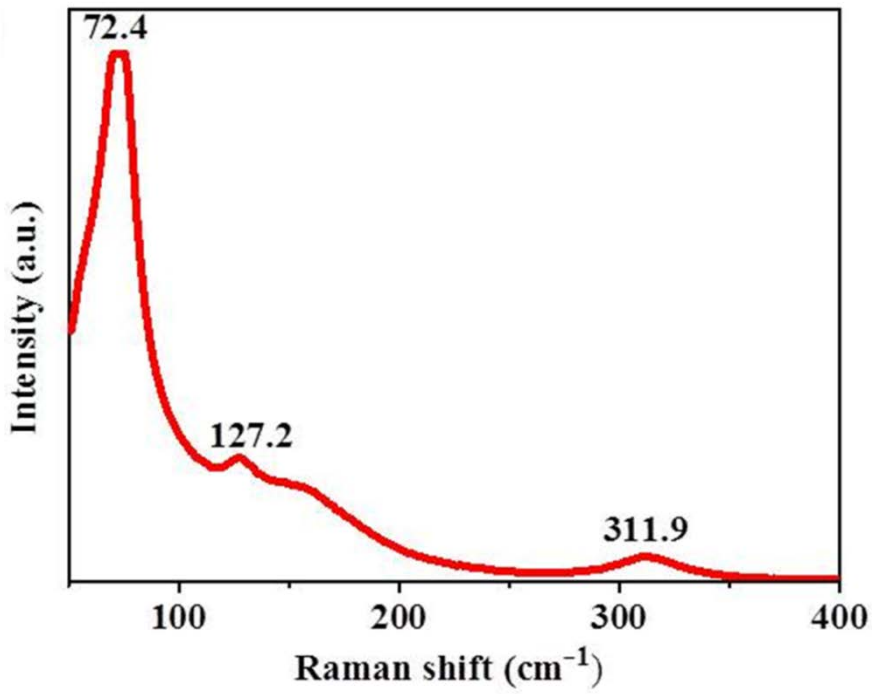

Figure S5. Raman spectrum of cubic-phase CsPbBr3 single crystal.

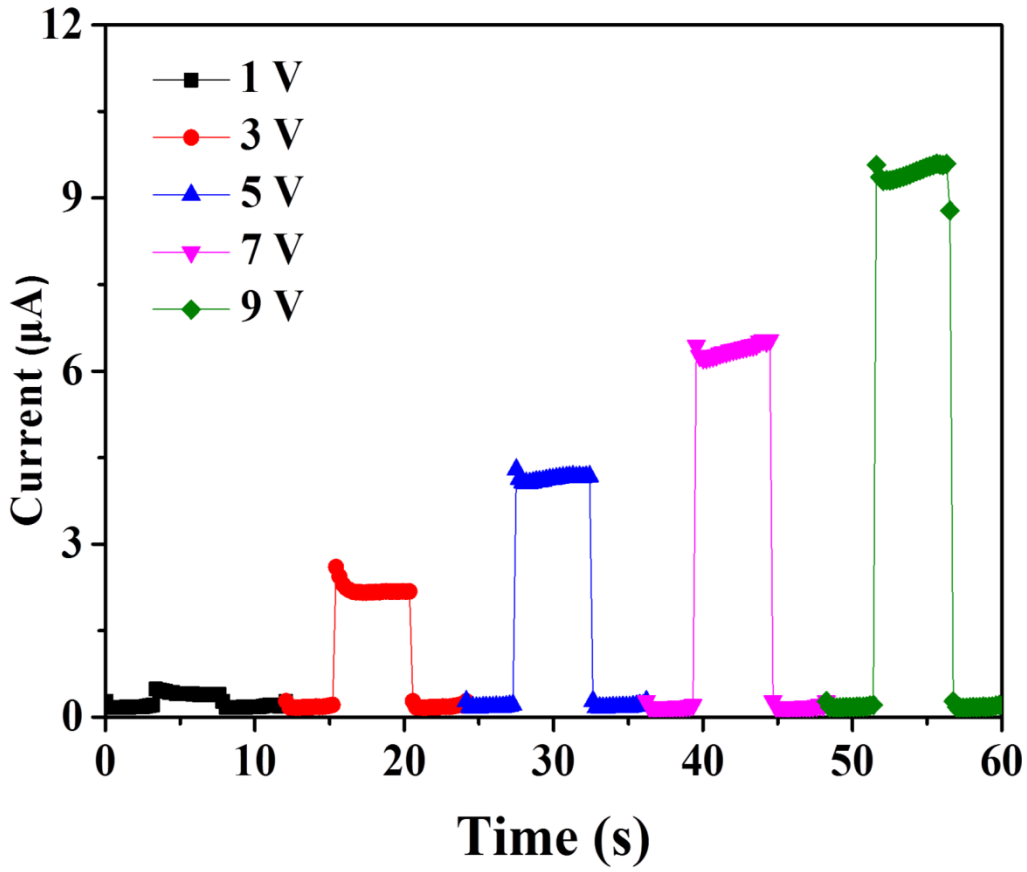

Figure S6. Current curves of the cubic-phase $CsPbBr_3$ single-crystal photodetector with at 1-9 V.

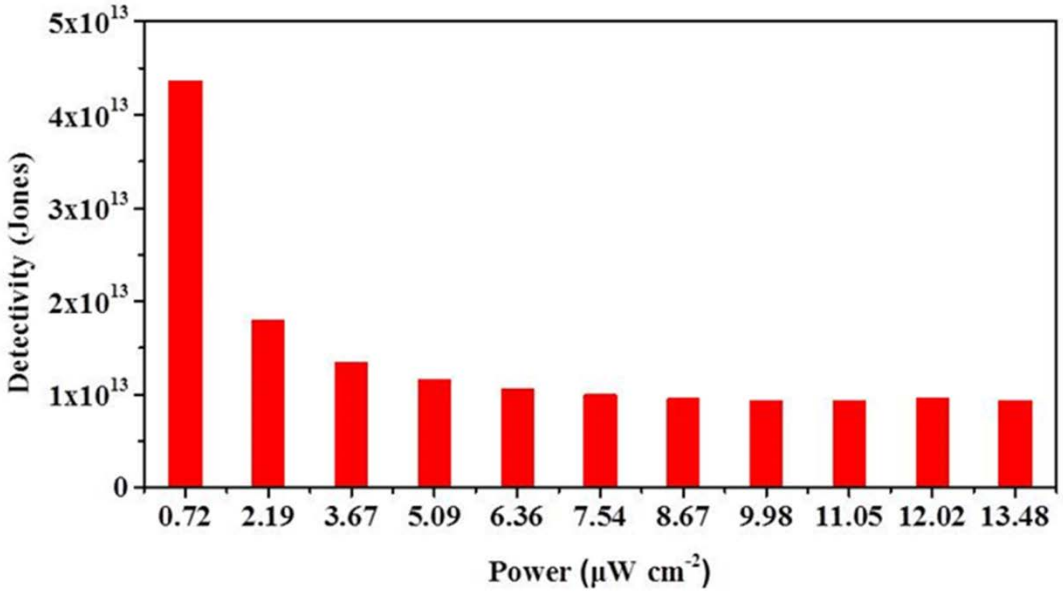

Figure S7. current−light intensity fitting curve for $CsPbBr_3$ single-crystal photodetector at different light intensities when the bias voltage is 3V and the light wavelength is 520 nm.

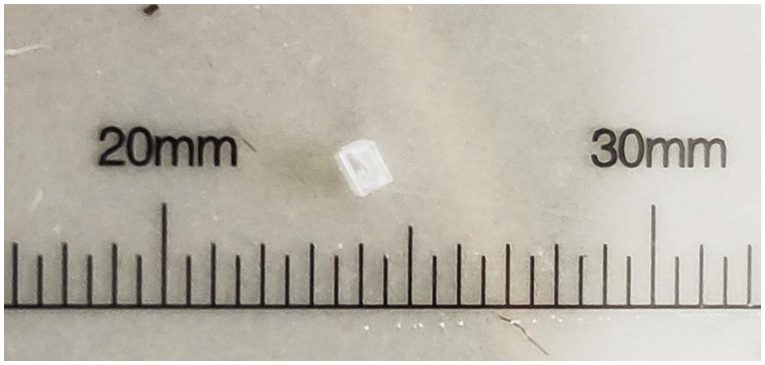

Figure S8. Photograph of $CsPbCl_3$ single crystal obtained with Cs/Pb of 1:1 in H2O/DMSO solution