

Single-Crystal Thin Films of Cesium Lead Bromide Perovskite

Epitaxially Grown on Metal Oxide Perovskite (SrTiO₃)

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Supporting Information

1. Experimental Section

1.1. Materials synthesis

All chemicals and reagents were purchased from Sigma-Aldrich and used as received unless noted otherwise. The dimethyl sulfoxide (DMSO) (Aldrich, $\geq 99.9\%$) and methanol (MeOH) (BioLab LTD, HPLC grade, 99.95%) solvents were also used as received. The SrTiO_3 (100) and SrTiO_3 (110) single-crystal substrates were purchased from MTI Corporation, USA. The dimension for the as-bought SrTiO_3 (STO) substrates is $10\text{ mm} \times 10\text{ mm} \times 0.5\text{ mm}$. The as-bought STO substrate was cut in half, which is $5\text{ mm} \times 10\text{ mm} \times 0.5\text{ mm}$, for one growth. The STO substrates were first etched by immersing in hot water ($80\text{ }^\circ\text{C}$, 60 min) and in buffered HF solution (2 min) sequentially, then washed with ultrapure deionized water ($18\text{ M}\Omega\cdot\text{cm}$) before crystal growth. Thus etched and cleaned STO substrate is believed to be atomically flat with Ti-O terminated surface.^{S1}

The growth of the epitaxial CsPbBr_3 nanoplates and single crystal thin films was carried out in a home-built “tube-in-tube” chemical vapor deposition (CVD) setup equipped with mass flow controllers and pressure control. The inner diameters of the outer tube and inner tube are 2.1 cm and 1.2 cm, respectively. This “tube-in-tube” setup with the sealed end of the inner tube facing the carrier gas flow direction helps to maintain a steady laminar flow in the reactor for controlled growth. CsPbBr_3 ingots were first prepared by melting CsBr and PbBr_2 (in 1:1 molar ratio) at $550\text{ }^\circ\text{C}$ under atmosphere pressure, and then used as the precursor for the epitaxial growth.

As illustrated in Figure S1, the CsPbBr_3 ingots were placed at the center of the heating zone inside the inner tube close to the sealed end of the inner tube. The SrTiO_3 (100) substrates were placed downstream at the cooling zone closer to the opening end of the inner tube. The distance between the precursor and the STO substrate was about 12 cm. Argon carrier gas was flown at 18 sccm and the pressure inside the CVD tube was maintained at 100 mTorr. For a typical growth of CsPbBr_3 nanoplate arrays, the CVD reactions were carried out for 60 min with the center of the heating zone (where the CsPbBr_3 precursor is at) set to $320\text{ }^\circ\text{C}$. For successful growth of continuous CsPbBr_3 single crystal thin films, the CVD reactions were run at $450\text{ }^\circ\text{C}$ (the temperature of the precursor) for 12-20 min, depending on the desired thickness. Once the reaction is finished, the furnace was turned off and allowed to cool naturally to room temperature.

We used slow anti-solvent vapor saturation to grow bulk CsPbBr_3 single crystals, following the procedure reported previously.^{S2} First, equimolar amounts of CsBr and PbBr_2 were dissolved in DMSO to produce a 0.45 M solution of the perovskite precursor in a 6 mL glass vial. Then this 6 mL vial was placed in a 24 mL vial which had been half-filled with MeOH (used as the anti-solvent) as illustrated in Figure S1c. Then this setup was kept in stable ambient environment for 3-5 days for the diffusion of the anti-solvent into the small vial until orange colored CsPbBr_3 single crystals were formed (see one single crystal in Figure S1c).

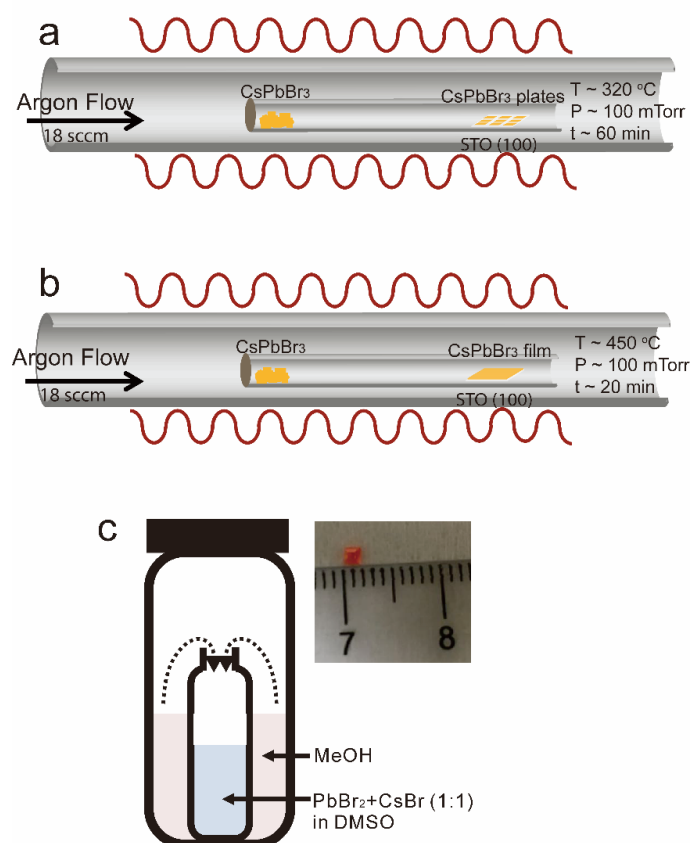


Figure S1. The tube-in-tube setup for the vapor phase epitaxial growth of the CsPbBr₃ nanoplates and single crystal thin films on STO substrates: (a) Growth of the CsPbBr₃ plates under relatively lower temperature (320°C), (b) Growth of CsPbBr₃ single crystal thin films under higher temperature (450°C). (c) The setup for the solution growth of CsPbBr₃ single crystals using slow anti-solvent vapor saturation.

1.2. Structural and Property Characterizations

The optical images of CsPbBr₃ plates were obtained on an Olympus BX51M optical microscope. The scanning electron microscopy (SEM) images were collected on a LEO SUPRA 55 VP field-emission scanning electron microscope operated at 3 kV. The PXRD data were collected on as-grown samples on substrates using a Bruker D8 Advance Powder X-ray Diffractometer with the Cu K α radiation. The XRD θ -rocking curve and pole figure were obtained on a Bruker D8 Discovery Diffractometer equipped with a specimen rotating holder. Atomic Force Microscope (AFM) imaging was performed with an Agilent 5500 S4 AFM instrument in the contact mode using a sharp silicon tip on nitride lever with reflective gold back coating, SNL-10 from Bruker AFM Probes, k: 0.12 N/m). We estimated the root mean-squared roughness (S_q) of the CsPbBr₃ SCTF by analyzing AFM images using the software “Gwyddion”. The photoluminescence (PL) spectra were collected with an Aramis Confocal Raman microscope using a 442 nm laser source with a neutral density filter D4. To clarify, we took the 7 μ m thick SCTF as the representative sample for XRD pole figure and all the following measurement described below.

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Time-resolved PL (TRPL) measurements were performed with a streak camera (C10910, Hamamatsu) using a laser pulses at 400 nm (repetition rate of 80 MHz, pulse width of 80 fs) as the light source. The 400 nm laser output was generated by an 800 nm laser from a mode-locked oscillator (Tsunami 3941-X1BB, Spectra-Physics) after a BBO crystal. The laser beam was focused by an objective lens (50 $\times$, Zeiss, 0.75NA) on the sample/substrate while PL emissions were collected by the same objective lens. The TRPL decay constant of 370 ps was obtained by fitting the transient to a monoexponential decay function after deconvolution of the Impulse Response Function (IRF).

For the ultrafast transient reflection (TR) spectroscopy, a regeneratively amplified, Ti:Sapphire laser (Spectra-Physics, Spitfire Pro XP) produced 800 nm pulses with ~ 35 fs duration and 1 kHz repetition rate. The output was split and pumped both an optical parametric amplifier (Light Conversion, TOPAS-C), which made 485 nm light, and a home-built sapphire white-light (WL) generation apparatus. The OPA output was time-delayed by a motorized retro-reflector and then shone on the sample. The WL probe was passed through an 800 nm dichroic filter and focused onto the sample with a 1 m spherical mirror --- 2 $^\circ$ separation between pump and probe beams. At the sample, the unfocussed pump (1.52 mm FWHM) provided a spatially uniform fluence ($14 \mu\text{J}/\text{cm}^2$, $N \approx 10^{18} \text{ cm}^{-3}$) for the focused probe (0.66 mm FWHM). The incident probe had a total energy of 17 nJ per pulse. The reflected probe light was coupled to a scanning monochromator and detected with an uncooled PMT (Hamamatsu 1P28A).

The device for electrical measurements was directly fabricated with an as-prepared 7 μm thick CsPbBr₃ single crystal thin film sample that had been grown at 450 $^\circ\text{C}$ for 20 min on SrTiO₃ (100) substrate. A shadow mask (50 μm features, purchased from Ossila, Ltd, U. K.) was used to cover the sample during metal evaporation to define a 1 mm long and ca. 50 μm wide electrode gap (that can be used as the illumination area in a photodetector device). Au electrode (~ 100 nm thick) was thermally evaporated through this shadow mask to make conductive contact. The dark I-V and photocurrent of the CsPbBr₃ single crystal thin film device were measured using a home-built electrical transport setup on a probe station (Cascade Microtech, RF-1 probe station) illuminated with a 150 W fiber optic illuminator (Technique, FOI-150). The light intensity was calibrated with a Si photodiode (Thorlabs). Voltages were sourced through a DAQ BNC-2090 terminal block (National Instruments) and the currents were amplified using a Model 1211 current pre-amplifier (DL Instruments) at a sensitivity of 10^{-4} A/V and measured through a computer-controlled National Instruments DAC card.

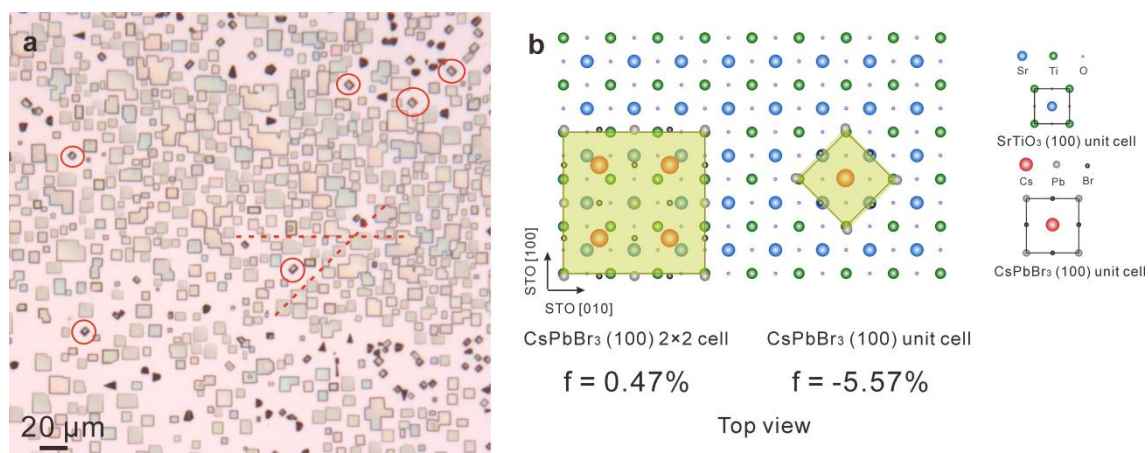
2. Supporting data for epitaxial growth of CsPbBr₃

Figure S2. (a) Large area optical microscopy image of the CsPbBr₃ plates on STO (100) substrate grown at 320 °C for 60 min. The red circles mark the less thermodynamically favorable orientation. (b) The corresponding schematic lattice match diagram calculated taking the lowest f factor and smallest overlapping unit cell area between the CsPbBr₃ and STO structures.

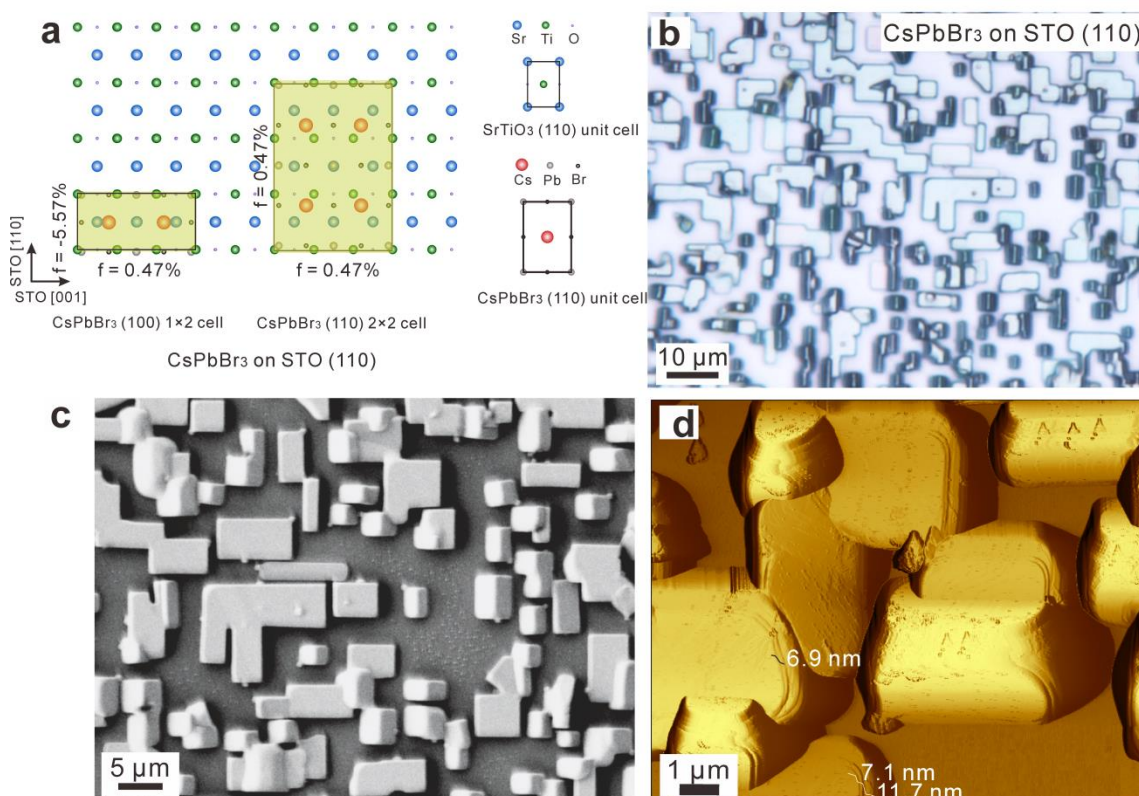


Figure S3. The epitaxial growth of CsPbBr₃ on STO (110) substrate grown at 320 °C for 60 min. (a) Illustration of the two possible lattice match arrangements between the CsPbBr₃ and STO (110). (b) Optical microscopy image, (c) SEM image, and (d) representative AFM of the CsPbBr₃ prisms and plates epitaxially grown on STO (110) substrate.

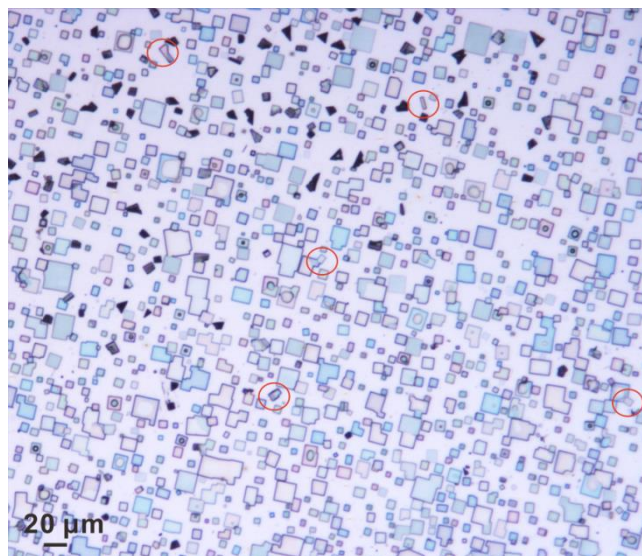


Figure S4. Optical microscopy image of the CsPbBr₃ plates on STO (100) grown at 320 °C for 90 min. It shows various morphologies, including the plates with orientation of {CsPbBr₃ [100] || STO [100], CsPbBr₃ [010] || STO [010]} and {CsPbBr₃ [100] || STO [110], CsPbBr₃ [010] || STO [110]} as well as many unorientated morphologies. The red circles mark less thermodynamically favorable orientation.

As shown in Figure S5, the thicker end of the 7 μm thick SCTF is at least 500 μm in length, meaning that we can at least grow a SCTF of 0.25 mm². This is larger than the reported works of halide perovskite (MAPbBr₃) SCTF growth.^{S3} On the other hand, as shown in Figure 2b, the thinner end of the 7 μm thick SCTF still has a thickness of 4.7 μm. All in all, the present SCTF has slight film thickness variation but it is not very large and it can be solved if using a bigger CVD reactor or tilting the substrate to a certain degree. The film is uniform in a relatively large area of up to at least hundreds of micrometers.

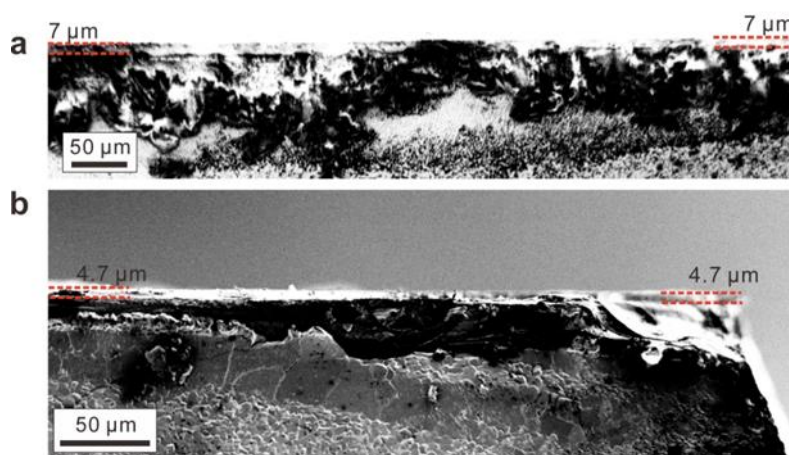


Figure S5. The large-scale SEM cross section images of the 7 μm thick SCTF on the thicker end (a) and on the thinner end (b).

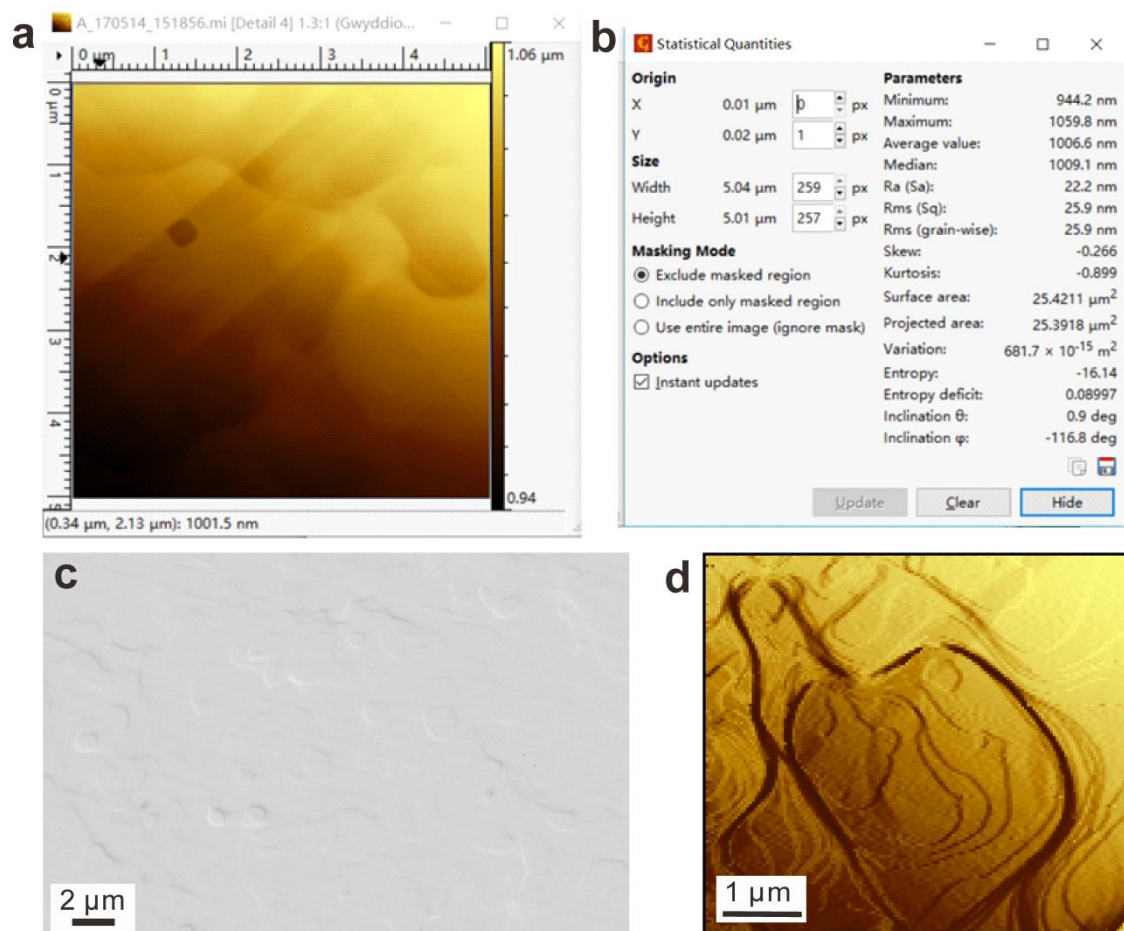


Figure S6. (a) AFM image of the surface highlighting a concave feature on the 7 μm thick CsPbBr_3 SCTF. (b) The raw data for determining the surface roughness of the 7 μm thick CsPbBr_3 SCTF by analyzing AFM image in (a) using the software “Gwyddion”. (c) SEM image of the 1 μm CsPbBr_3 single crystal thin film showing some surface textures. (d) AFM image of the surface highlighting a concave feature on this 1 μm thick CsPbBr_3 single crystal thin film. These concave structures were observed on the thin film as well as on the thicker nanoplates after longer growth time, which highly suggests that the concave structures come with growth rather than etching.

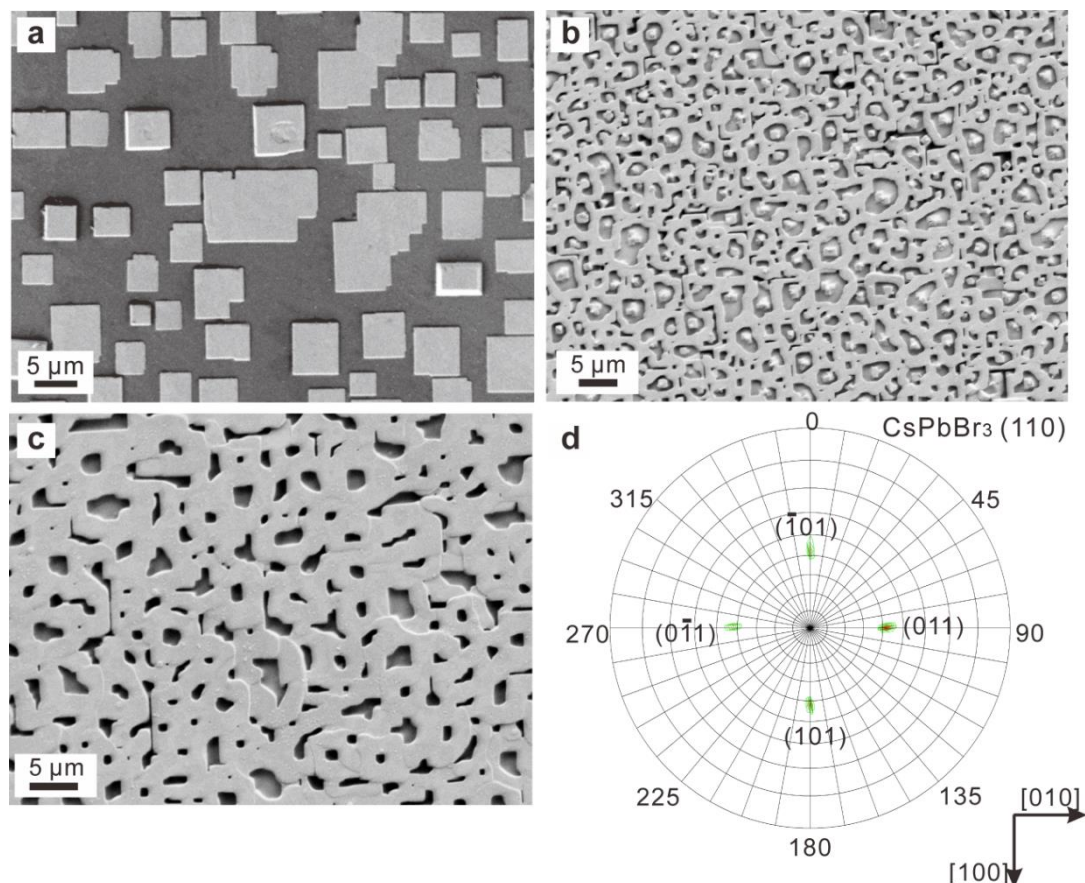


Figure S7. (a) SEM image of the CsPbBr_3 plates grown on STO (100) substrate at 320 °C for 60 min. (b) SEM image of the CsPbBr_3 nanostructures grown at 450 °C for 7 min on STO (100) substrate. (c) SEM image of the CsPbBr_3 nanostructures grown at 450 °C for 10 min on STO (100) substrate. (d) The (110) pole figure of the 10 min sample of $\text{CsPbBr}_3/\text{STO}$ (100) in panel c, confirming the single crystallographic orientation epitaxial growth, just like what was observed for SCTF samples.

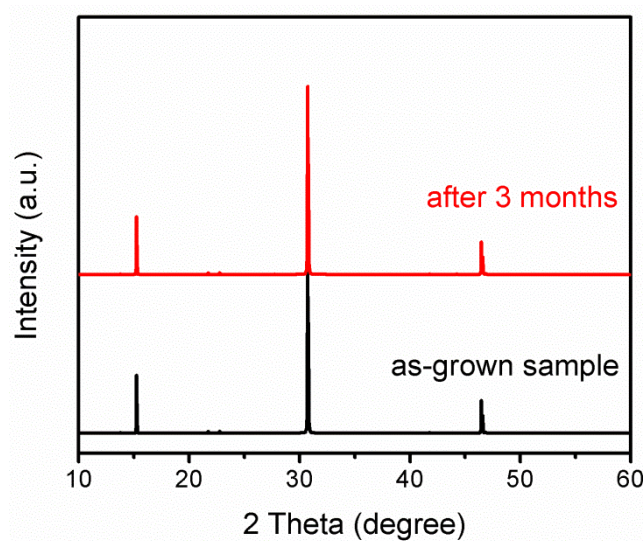


Figure S8. XRD patterns of the as-grown CsPbBr_3 SCTF in comparison with the PXRD pattern taken after the sample was stored in ambient condition for 3 months.

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Table S1. The reported PL lifetime values on CsPbBr₃ single-crystalline materials.

CsPbBr ₃ Materials	Preparation methods	Excitation wavelength	Lifetime τ_1 ns (ratio)	Lifetime τ_2 ns (ratio)	Ref
Single crystal	Anti-solvent	442 nm	10.7	/	This work
Single crystal thin film	VPE	442 nm	10.5	/	This work
NWs (tens of nm)	colloidal	402 nm	1.22 (74%)	3.55 (26%)	S4
Large single crystal	Anti-solvent	/	1.20 (83.5%)	8.65 (16.5%)	S5
Large single crystal	Anti-solvent	400 nm	4.4 $\pm$ 0.1	30 $\pm$ 3	S2
Large single crystal	solution method	800 nm	23	233	S6
Single crystal ingot	Bridgman method	442 nm or 800 nm	Average τ : 8.5 (442 nm); 10.5 (800 nm)		S7
Nanocrystals (several nm)	colloidal	/	The larger τ is 15 ns		S8

3. Supporting data for TR spectroscopy

The supporting information for the TR results is organized as follows:

- (a) Exposition on the diffusion model used to expose surface dynamics of the samples;
- (b) Raw data showing the probe frequency vs. time response of the materials;
- (c) Discussion and representation of the SVD analysis used to extract temporal transients from the raw data;
- (d) Discussion and representation of the fitting accomplished;
- (e) Temporal traces of the slab for different pump fluences.

3.1 Diffusion model

We posit that our excited carriers evolve according to Fick's second law,

$$\frac{\partial N(z, t)}{\partial t} = D \nabla^2 N(z, t),$$

where D is the diffusion coefficient and N is the carrier density. Because our pump beam is much larger than our probe beam, we further assume all diffusion occurs exclusively in the z direction. The initial condition for our diffusion problem is the carrier distribution defined by the pump excitation $N(z, t = 0) \propto \exp(-\alpha z)$ in which α is the absorption coefficient at our pump energy, $\alpha(\hbar\omega = 2.56 \text{ eV}) = 0.434 \times 10^5 \text{ cm}^{-1}$, which we take from De Roo et al.^{S9} We impose two boundary conditions on our system:

1. At the excited surface, the recombination flux is proportional to surface density.

$$J(z = 0, t) = -SN(z = 0, t)$$

Substitution of Fick's first law then yields

$$-D \nabla N(z = 0, t) = -SN(z = 0, t)$$

upon rearrangement we arrive at the boundary condition used by many in the literature

$$\left. \frac{\partial N(z, t)}{\partial z} \right|_{z=0} = \frac{S}{D} N(z = 0, t)$$

2. The sample is 7 μm thick, which is thick enough that the back surface is not relevant. In equation form

$$N(z = \infty, t) = 0$$

This assumption is valid because the attenuation coefficient of our pump beam implies a 1/e length of $\sim 0.2 \mu\text{m}$ and the VPE grown SCTF has a thickness of $\sim 7 \mu\text{m}$, so created carriers (in the first nanosecond of evolution) will not be able to reach the back of the VPE grown SCTF. Consider: $\langle r \rangle = \sqrt{Dt} \approx \sqrt{1 \frac{\text{cm}^2}{\text{s}} \cdot 1 \text{ ns}} = 0.03 \mu\text{m}$. Thus carriers move ~ 0.03 microns in the first nanosecond. Hence, no carriers will reach the back of our samples within the timescale of our experiments.

Given all of the above conditions, our system will evolve as the following known solution.^{S10}

$$N(z, t) = \frac{N_0}{2} e^{(-\frac{z^2}{4Dt})} \left\{ W\left(\alpha\sqrt{Dt} - \frac{z}{2\sqrt{Dt}}\right) + W\left(\alpha\sqrt{Dt} + \frac{z}{2\sqrt{Dt}}\right) - \frac{2\frac{S}{D}}{\frac{S}{D} - \alpha} \left[W\left(\alpha\sqrt{Dt} + \frac{z}{2\sqrt{Dt}}\right) - W\left(\frac{S}{D}\sqrt{Dt} + \frac{z}{2\sqrt{Dt}}\right) \right] \right\}$$

in which we have defined $W(X) \equiv \exp(X^2)[1 - \text{erf}(X)]$

Next, we assume our probe only interacts with carriers at the surface of the material.^{S11} With all assumptions and conditions in place, our system will undergo diffusion according to the following known solution.

$$\text{signal} \propto N(z = 0, t) = N_0 \left\{ W(\alpha\sqrt{Dt}) - \frac{\frac{S}{D}}{\frac{S}{D} - \alpha} \left[W(\alpha\sqrt{Dt}) - W\left(\frac{S}{D}\sqrt{Dt}\right) \right] \right\}$$

3.2 Raw data

Our primary TR dataset consists of three probe frequency vs. delay time 2D experiments for each sample. The results of these six, sequential experiments are shown below in Figure S9. No normalization or smoothing was imposed. We observe a small shift (~ 20 meV) between the two samples in the zero-crossing of the dispersive lineshape. This difference could be due to the Fresnel interference of the thin film, which has dramatically affected band-edge TR spectra in other thin film perovskites.^{S11} The speckled response in the higher frequency range of the experiment is due to large relative variations of probe intensity for those colors.

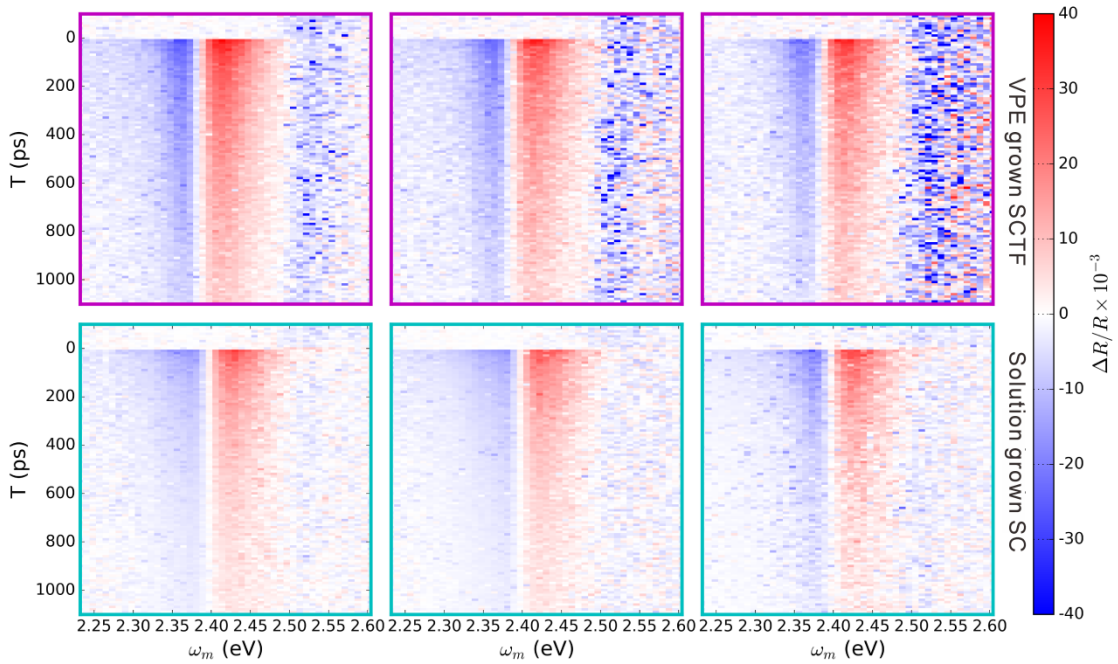


Figure S9. Raw data of the TR spectroscopy collected on the two types of CsPbBr₃ samples: vapor-phase epitaxial growth single crystal thin film (SCTF) and solution grown single

crystal (SC).

3.3 Spectrum Fitting

Prior to fitting, singular value decomposition (SVD) was used to suppress random noise and to reduce the fit dimensionality^{S12}. We found that for both the SCTF and the SC, the data were well-described by the first singular value, shown in Figure S10. Figure S10 clearly shows that TR spectra of the two CsPbBr₃ samples are frequency shifted, as also can be seen in the raw data.

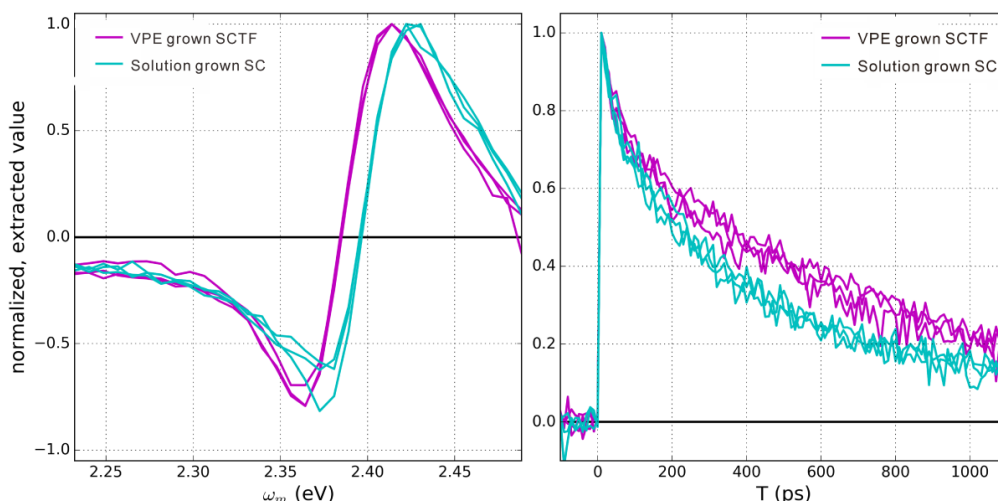


Figure S10. First singular vectors extracted from raw data.

Following SVD, we averaged the three temporal singular vectors for each sample and fit them to the diffusion model described above using a linear least squares algorithm. We found the exact value of S and D for each fit to be quite sensitive to the noise of the data, which is why we originally accomplished the SVD extraction. The covariance matrices for the two fits are shown below. The square-root of the diagonal elements gives the standard deviation of the fit parameter which corresponds to the row and column of the element.

Table S2 Covariance matrices for linear least squares fit. Units of S and D are given in the body: cm/s and cm²/s, respectively. Units of N are arbitrary due to normalization following SVD.

	VPE grown single crystal thin film			Solution grown single crystal		
	S	D	N0	S	D	N0
S	2.48E+6	-7.67E+4	-3.63E+1	2.63E+6	-8.21E+4	-2.96E+1
D	-7.67E+4	2.67E+3	1.56E+0	-8.21E+4	3.85E+3	2.21E+0
N0	-3.63E+1	1.56E+0	1.22E-3	-2.96E+1	2.21E+0	1.70E-3

Below in Figure S11, we show a representation in which we set the values of S and D and then calculate the root-mean-square error (RMS) between the model and the data. A wide range of values for each parameter give reasonable errors, and the values are correlated in such a way that a small increase in D can be offset by a small decrease in S . Given a data

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set with slightly different random noise, we could have fit to a vastly different value of S and D . However, the main take-away still stands: the surface recombination velocity between the two samples differ. Observe how the solution grown SC's RMS error balloons as S values of 15000 cm/s are approached. The VPE grown SCTF has the same behavior as S values of 30000 cm/s are approached. This entails that the two values of S must differ.

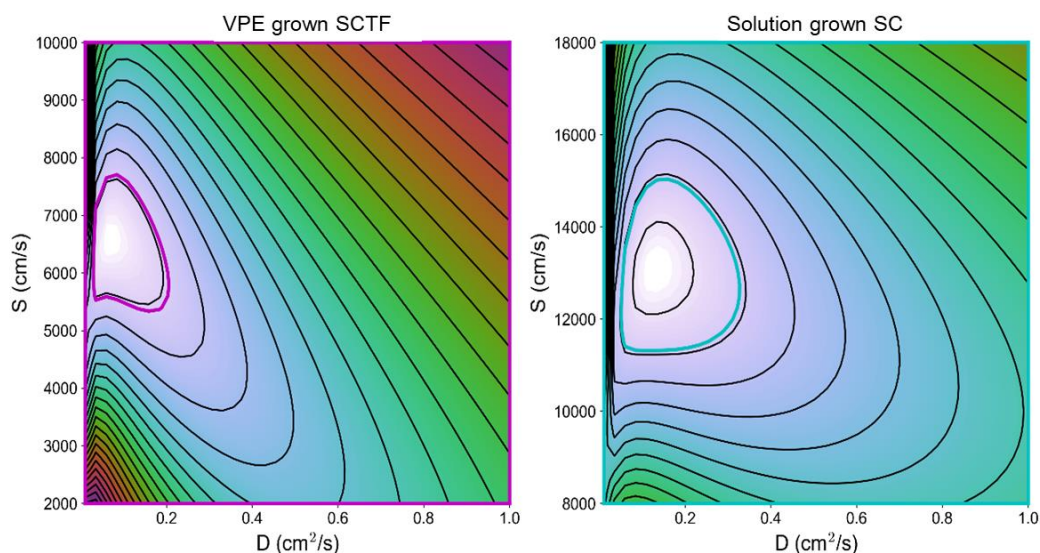


Figure S11. Exploration of the fitting errors. Color bar is RMS value after fit. White is lowest error. The bold, colored contour line shows a 10% increase of RMS error from the minimum RMS error.

3.4 Fluence study

Below in Figure S12, we show 6 delay traces at different pump fluences. As the fluence is decreased, the signal-to-noise ratio decreases. We see a roughly linear trend of the max signal as a function of fluence. This implies we are in a linear-fluence regime.

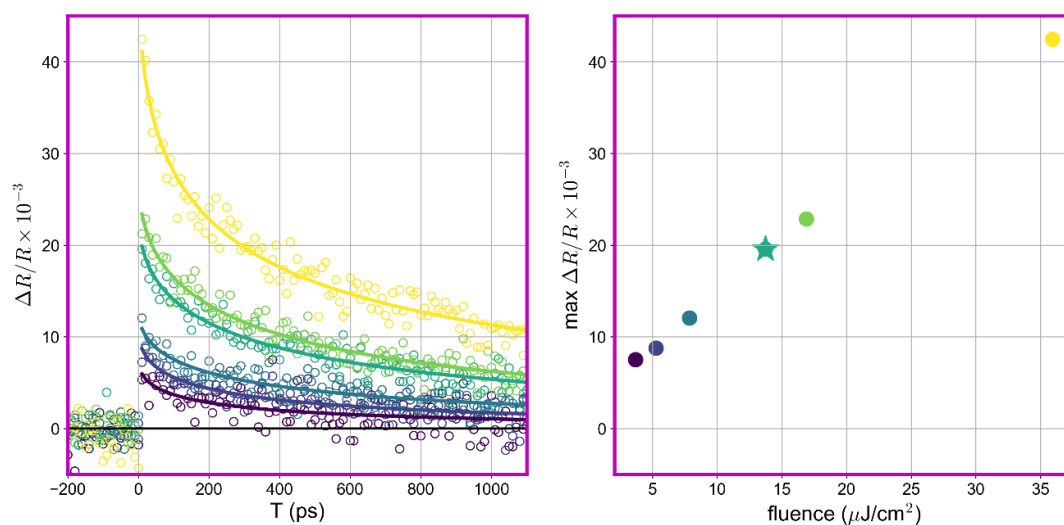


Figure S12. (left) TR response of a CsPbBr₃ SCTF vs. delay for 6 different pump fluences. Solid lines are guides to the eye. (right) maximum response vs. pump fluence. The star

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scatter-point marks the fluence at which all fitted data were acquired.

4. Supporting data for electron transport and photocurrent measurement

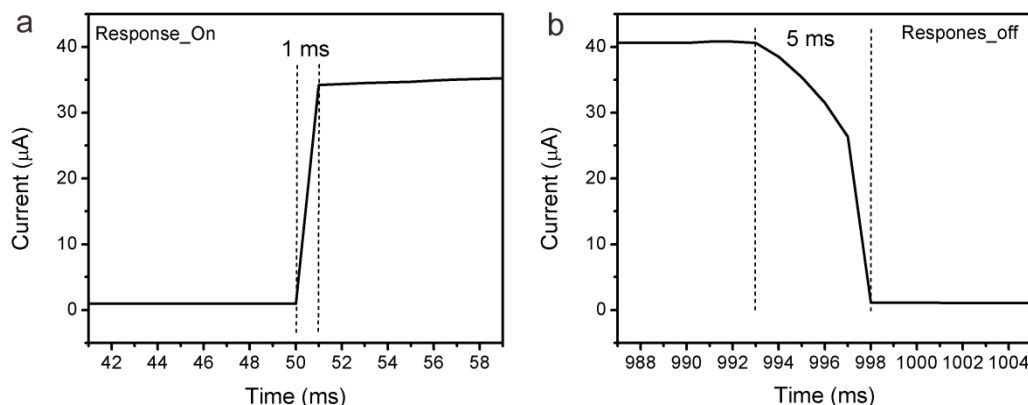


Figure S13. The on and off photocurrent response the Au/CsPbBr₃/Au device highlighting the fast (within several ms) response of the photodetector device based on CsPbBr₃ SCTF.

Table S3. Summary of the trap state density (n_t) values of the CsPbBr₃ single-crystalline materials.

CsPbBr ₃ Materials	Preparation methods	Configuration	Trap state density (n_t) cm ⁻³	Ref
Single crystal thin film	VPE	Au/CsPbBr ₃ film/Au (lateral)	1.5×10^{12}	This work
NWs (tens of nm)	colloidal	Au/CsPbBr ₃ NW/Au (lateral)	$10^{14} - 10^{15}$	S4
Single crystal ingot	Bridgman method	Au/CsPbBr ₃ ingot/Au (vertical)	1.9×10^9	S7
Single crystal	Solution method	Au/CsPbBr ₃ crystal/Au (vertical)	10^{10}	S6

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