

Supporting Information for:

All-Inorganic Perovskite Solar Cells

Jia Liang,[†] Caixing Wang,[†] Yanrong Wang,[†] Zhaoran Xu,[†] Zhipeng Lu,[†] Yue Ma,[†] Hongfei Zhu,[†] Yi Hu,[†] Chengcan Xiao,[†] Xu Yi,[†] Guoyin Zhu,[†] Hongling Lv,[†] Lianbo Ma,[†] Tao Chen,[†] Zuoxiu Tie,[†] Zhong Jin,^{†,*} and Jie Liu^{†,‡,*}

[†] Key Laboratory of Mesoscopic Chemistry of MOE and Collaborative Innovation Center of Chemistry for Life Sciences, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, Jiangsu 210093, China

[‡]Department of Chemistry, Duke University, Durham, North Carolina 27708, USA

*Correspondence and requests for materials should be addressed to Z. J. (email: zhongjin@nju.edu.cn) or J. L. (email: j.liu@duke.edu)

Methods

Preparation of CsPbBr₃/carbon based all-inorganic PSCs

All the fabrication steps of CsPbBr₃/carbon based PSCs were conducted in ambient air. Commercially-available FTO glass (with the FTO thickness of ~1 μm) was firstly etched by Zn powder and 2.0 M HCl for desirable patterns and then sequentially cleaned with acetone, ethanol, and deionized water. The c-TiO₂ layer was deposited on FTO substrate by spin-coating an ethanol solution of titanium isopropoxide (0.5 M) and diethanol amine (0.5 M) at 7000 rpm for 30 s and annealing in air at 500 °C for 2 h. The m-TiO₂ layer was then deposited by spin-coating a mixture of TiO₂ paste (with average particle size of 20 nm) and ethanol with a weight ratio of 1:8 at 5000 rpm for 30 s, dried at 120 °C for 10 min and annealed in air at 500 °C for 30 min. Then the substrate was immersed in an aqueous solution of 0.04 M TiCl₄ at 70 °C for 30 min, cleaned with water and ethanol, and then annealed at 450 °C for another 30 min. Subsequently, a N,N-dimethylformamide (DMF) solution of 1.0 M PbBr₂ was spin-coated onto the m-TiO₂ layer at 2000 rpm for 30 s, followed by drying at 80 °C for 30 min. Then the substrate was dipped in a methanol solution of 0.07 M CsBr for 10 min, rinsed with isopropanol, dried in air, and heated to 250 °C for 5 min on a hotplate to form a uniform layer of CsPbBr₃. Finally, the carbon electrode served as both HTM and counter electrode was deposited on the CsPbBr₃ layer by doctor-blade coating of conductive carbon ink and then heated at 70 °C for 60 min.

Preparation of MAPbI₃/carbon and MAPbI₃/spiro-MeOTAD based hybrid PSCs as control devices

Due to the instability of MAPbI₃, the fabrication of MAPbI₃/carbon based hybrid PSCs was operated in Ar-filled glovebox. The procedure for the deposition of MAPbI₃ film was similar to that of CsPbBr₃ film, except for the precursors of PbBr₂ and CsBr were replaced by PbI₂ and methylammonium iodide (MAI), respectively. After the reaction of PbI₂ and MAI, the MAPbI₃/TiO₂ film was annealed at 70 °C for 30 min instead of 250 °C.

MAPbI₃/Spiro-MeOTAD based hybrid PSCs with the structure of FTO/c-TiO₂/m-TiO₂/MAPbI₃/spiro-MeOTAD/carbon were also fabricated in Ar-filled glovebox. All the functional layers were deposited with the same procedures of above MAPbI₃/carbon based hybrid PSCs, except for an additional HTM layer of spiro-MeOTAD was deposited by spin-coating at 4000 rpm for 30 s before the deposition of carbon electrode.

Preparation of CsPbI₃/carbon based all-inorganic PSCs as control devices

Different from CsPbBr₃, the fabrication of CsPbI₃/carbon based all-inorganic PSCs was operated in Ar-filled glovebox. The deposition procedure of CsPbI₃ film was also similar to that of CsPbBr₃ film, except for PbBr₂ and CsBr were replaced by PbI₂ and CsI, respectively. After the reaction of PbI₂ and CsI, the substrate was heated at 335 °C for 5 min to obtain cubic-phase CsPbI₃ film instead of 250 °C.

Characterizations

XRD spectra were collected with a Bruker D-8 Advance diffractometer using Cu K α X-ray radiation. The absorbance spectra of inorganic perovskite films were measured using a Shinadzu

UV-2456 spectrophotometer. SEM characterizations were performed on a HITACH S-4800 instrument. AFM characterizations were conducted on a Bruker Dimension Icon with tapping mode in ambient atmosphere. Raman spectra were obtained with a Horiba JY Evolution Raman spectrometer using a 473 nm laser source. XPS analysis was performed on a PHI-5000 VersaProbe X-ray photoelectron spectrometer with an Al $K\alpha$ X-ray radiation. The binding energies of elements and the valence band position of CsPbBr₃ film were determined by XPS.

The $J-V$ plots were measured with a Keithley 2400 Source Meter under AM 1.5G simulated solar illumination (100 mW/cm², NOWDATA SXDN-150E solar simulator). The light intensity was calibrated with a standard Si solar cell for 1 sun. Typically, the default active area of PSCs in this study is 0.12 cm². The incident photon-to-electric current conversion efficiency (IPCE) spectrum of the all-inorganic PSC with a large active area of 1.0 cm² was measured as a function of wavelength controlled by a monochromator. The stability of all-inorganic PSCs during temperature circles between -22 °C and 100 °C was also tested. Specifically, the working temperature was sequentially set at -22 °C, 10 °C, 40 °C, 70 °C, 100 °C, 70 °C, 40 °C, and 10 °C for 2 h, respectively, and the $J-V$ plots were measured at the end of each temperature step. The temperature circles were repeated for 5 times.

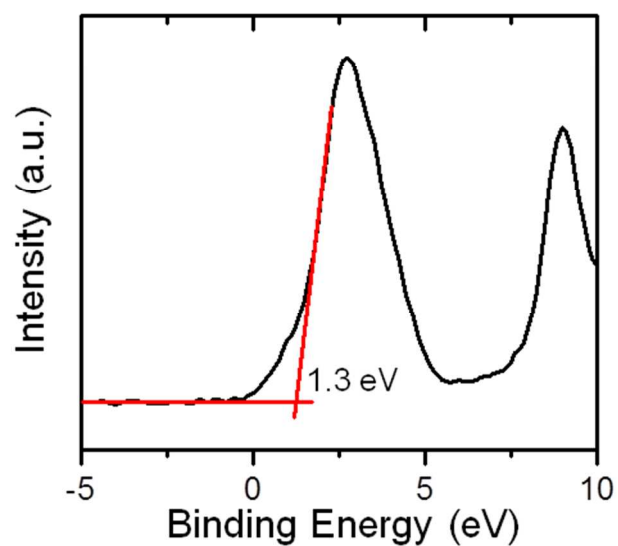


Figure S1. Valence band XPS spectrum of CsPbBr₃ film. The spectrometer work function of the XPS instrument used in this work is 4.3 eV. The valence band maximum (VBM) of CsPbBr₃ was determined by taking a linear extrapolation and was estimated to be 5.6 eV, as shown in **Figure S1**. Besides, **Figures 1e** and **f** indicate the optical bandgap of CsPbBr₃ is 2.3 eV. Thus, the conduction band minimum (CBM) of CsPbBr₃ film was calculated to be 3.3 eV.

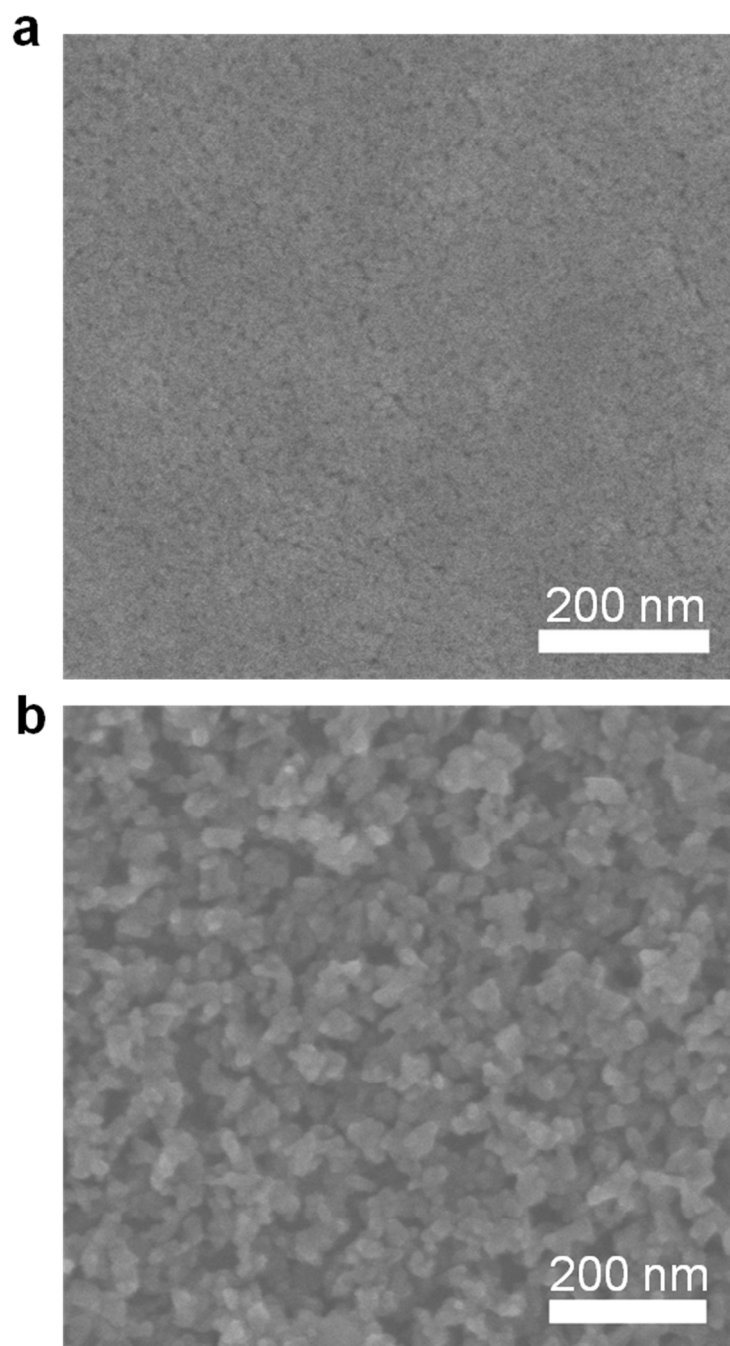


Figure S2. SEM characterizations. SEM images of (a) c-TiO₂ layer and (b) m-TiO₂ layer, respectively, confirming that m-TiO₂ nanoparticles with average diameter of ~20 nm were uniformly deposited on the c-TiO₂ layer.

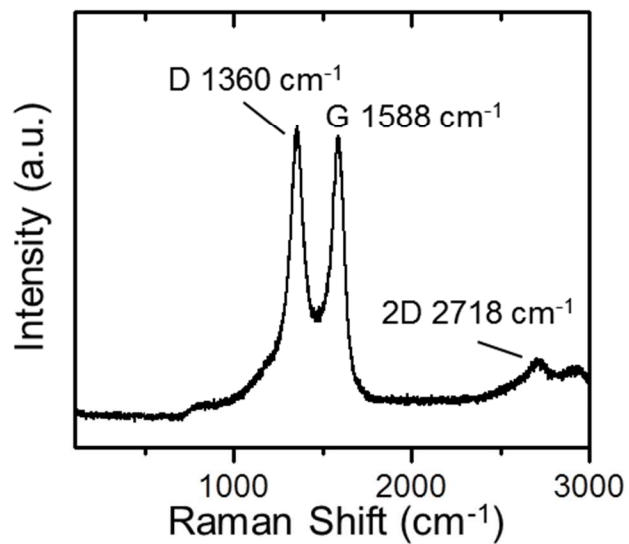


Figure S3. Raman characterization. Raman spectrum of the carbon electrode deposited on the CsPbBr₃ layer of all-inorganic PSCs.

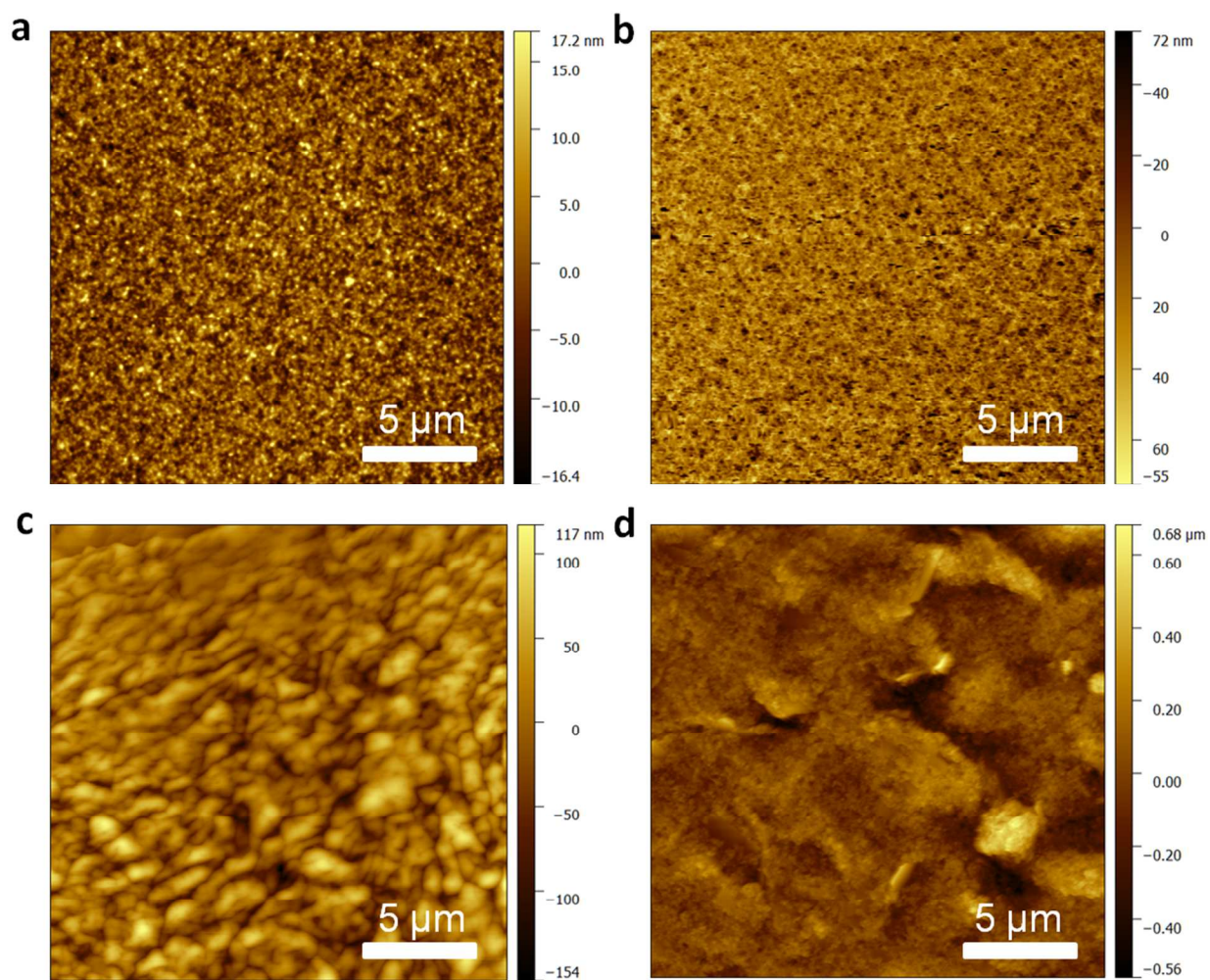


Figure S4. AFM characterizations. AFM images of (a) c-TiO₂ layer, (b) m-TiO₂ layer, (c) CsPbBr₃ layer and (d) carbon electrode, respectively.

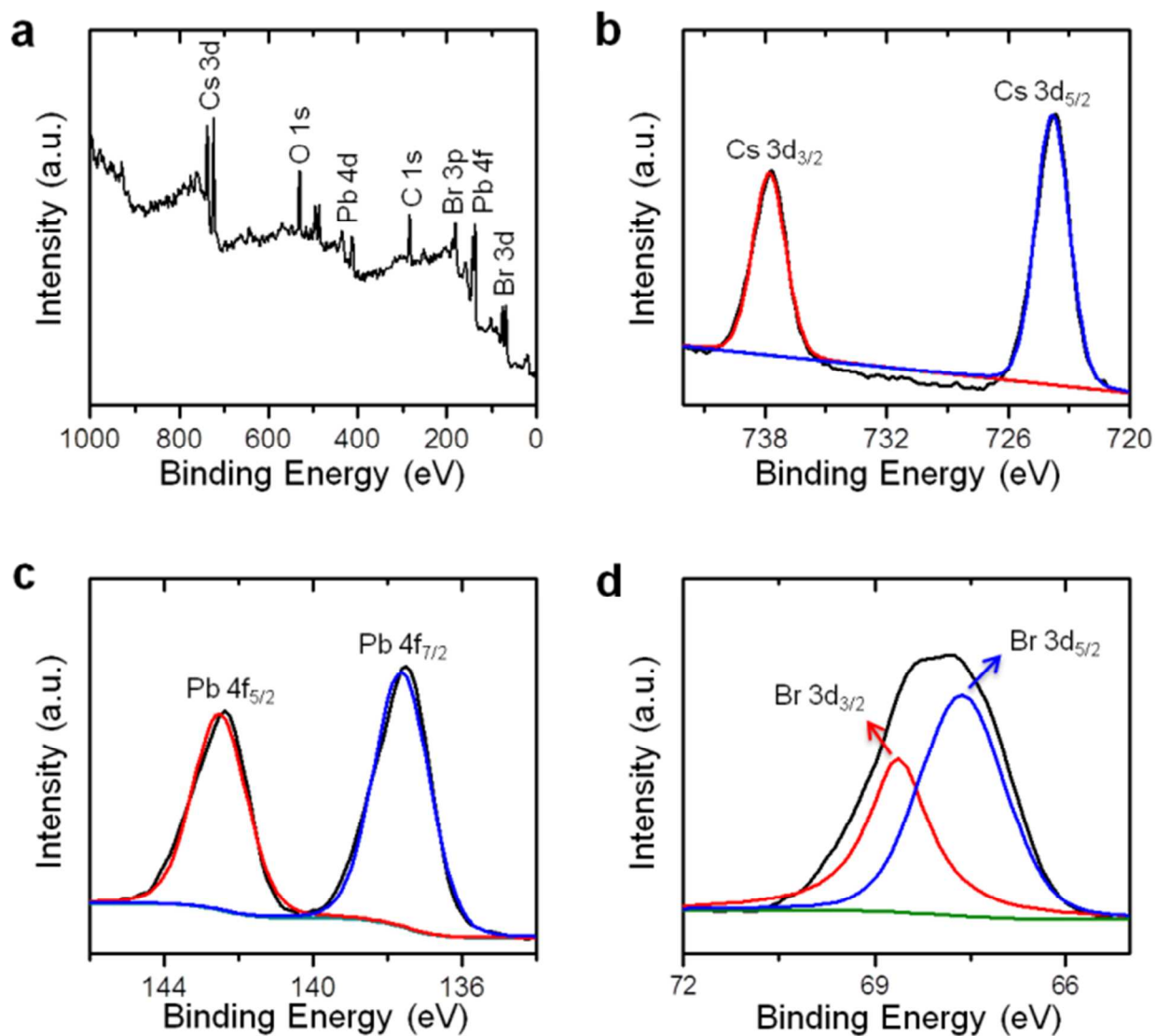


Figure S5. (a) Survey XPS spectrum of CsPbBr₃ film. (b-d) Corresponding high-resolution XPS spectra of the (b) Cs 3d, (c) Pb 4f and (d) Br 3d regions.

Table S1. XPS characterizations. XPS binding energies and atomic ratios of Cs, Pb and Br elements measured from the inorganic perovskite CsPbBr₃ layer, respectively.

	Cs 3d _{5/2}	Cs 3d _{3/2}	Pb 4f _{7/2}	Pb 4f _{5/2}	Br 3d _{5/2}	Br 3d _{3/2}
Binding Energy (eV)	723.6	737.6	137.5	142.4	67.6	68.6
Atomic Ratio (%)	21.2		22.5		56.3	

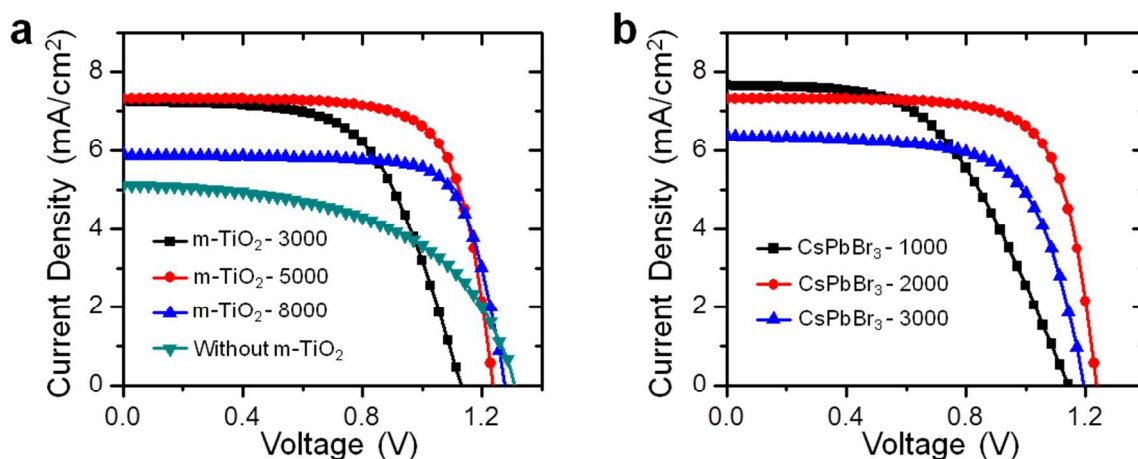


Figure S6. (a) J - V curves of CsPbBr₃/carbon based all-inorganic PSCs without m-TiO₂ layer and with different thicknesses of m-TiO₂ layer by adjusting the spin-coating rates of TiO₂/ethanol solution (3000, 5000 or 8000 rpm). (b) J - V curves of CsPbBr₃/carbon based all-inorganic PSCs with different thicknesses of CsPbBr₃ perovskite layer by adjusting the spin-coating rates of PbBr₂/DMF solution (1000, 2000 or 3000 rpm).

Table S2. Photovoltaic parameters of CsPbBr₃/carbon based all-inorganic PSCs without m-TiO₂ layer, with different thicknesses of m-TiO₂ layer by adjusting the spin-coating rates of TiO₂/ethanol solution (3000, 5000 or 8000 rpm), and with different thicknesses of CsPbBr₃ perovskite layer by adjusting the spin-coating rates of PbBr₂/DMF solution (1000, 2000 or 3000 rpm).

Spin-coating conditions		J_{SC}	V_{OC}	FF	PCE
CsPbBr ₃ -2000	m-TiO ₂ -3000	7.3	1.13	0.60	5.0
	m-TiO ₂ -5000	7.4	1.24	0.73	6.7
	m-TiO ₂ -8000	5.9	1.27	0.75	5.6
	Without m-TiO ₂	5.1	1.31	0.54	3.6
m-TiO ₂ -5000	CsPbBr ₃ -1000	7.7	1.14	0.52	4.6
	CsPbBr ₃ -2000	7.4	1.24	0.73	6.7
	CsPbBr ₃ -3000	6.4	1.19	0.67	5.1

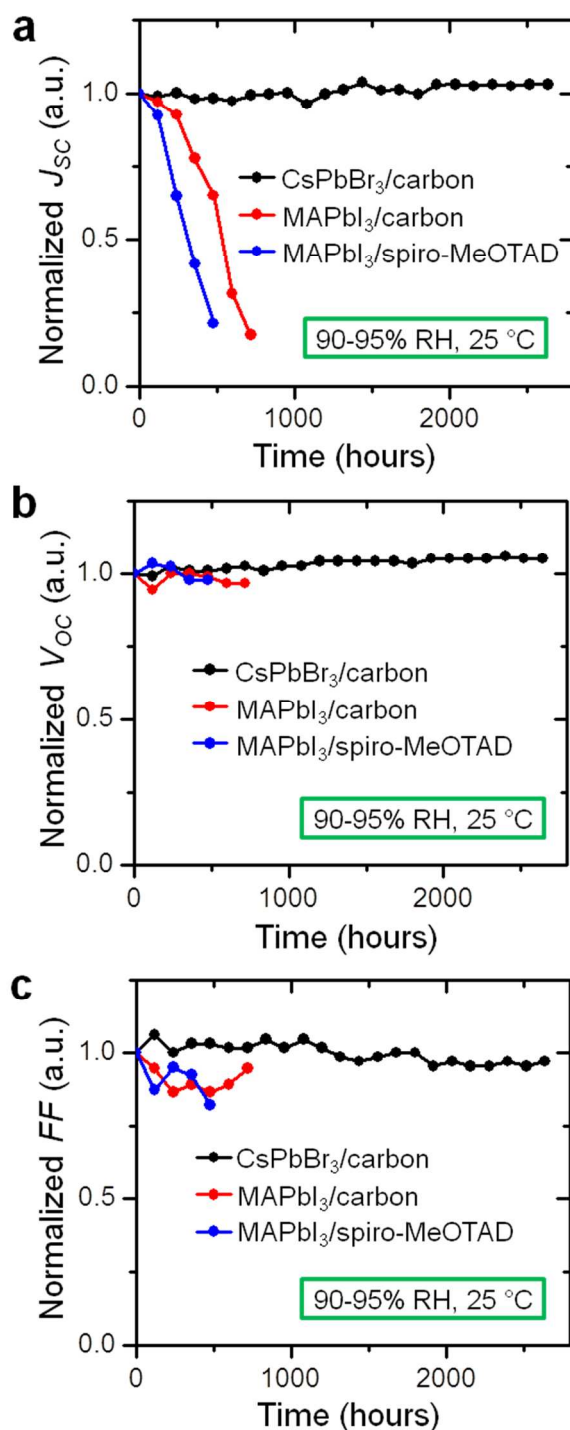


Figure S7. Stability comparisons of CsPbBr₃/carbon based all-inorganic PSCs with MAPbI₃ based hybrid PSCs in humid air. (a) Normalized J_{SC} , (b) V_{OC} and (c) FF of CsPbBr₃/carbon based all-inorganic PSCs, MAPbI₃/carbon and MAPbI₃/Spiro-MeOTAD based hybrid PSCs as a function of storage time in humid air (90-95% RH, 25 °C) without encapsulation, respectively.

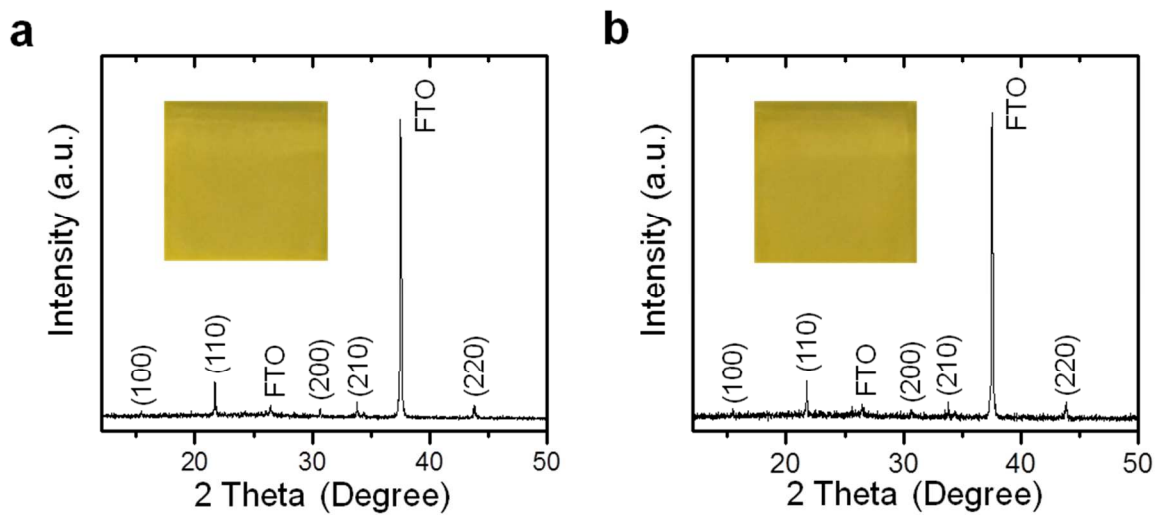


Figure S8. XRD characterizations and Photographs. XRD characterizations of bare CsPbBr₃ film (a) before and (b) after exposed in humid air (90-95% RH, 25 °C) for 15 days. The insets in (a) and (b) show the corresponding photographs. (The peaks marked by “FTO” represent the XRD peaks of FTO glass substrate).

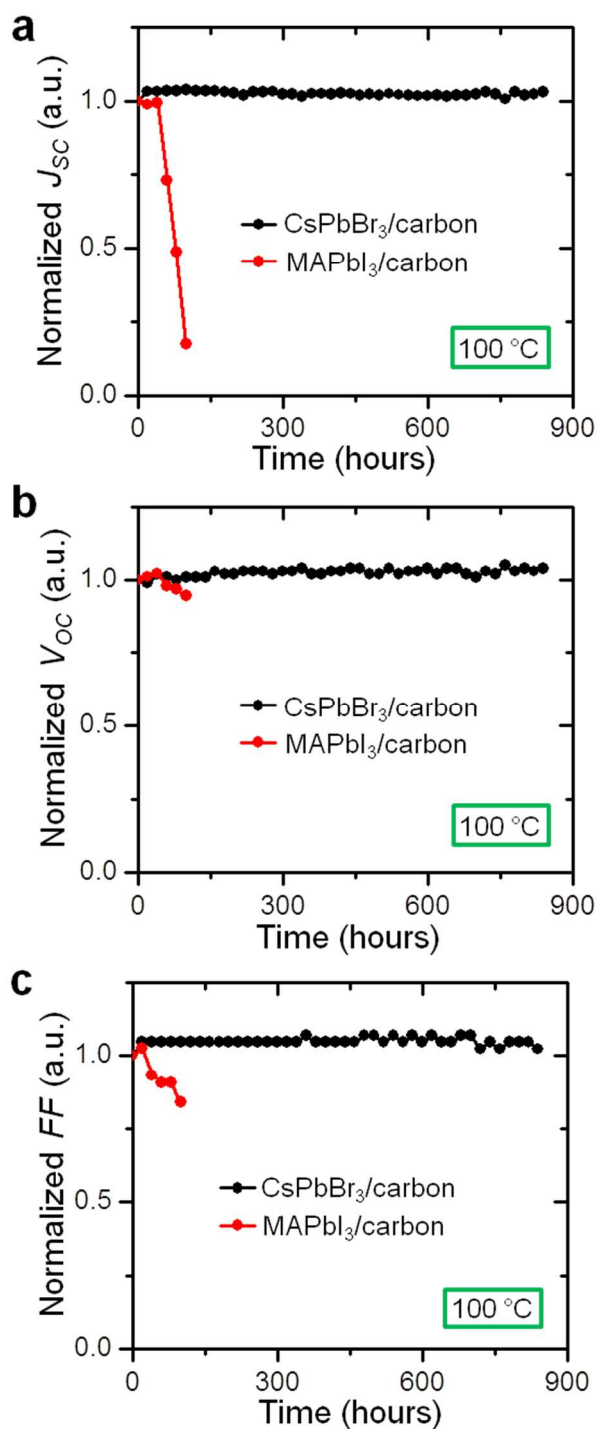


Figure S9. Stability comparisons of CsPbBr₃/carbon based all-inorganic PSCs with MAPbI₃ based hybrid PSCs at high temperature (100 °C) condition without encapsulation. (a) Normalized J_{SC} , (b) V_{OC} and (c) FF of CsPbBr₃/carbon based all-inorganic PSCs and MAPbI₃/carbon based hybrid PSCs as a function of time heated at high temperature (100 °C) in high-humidity ambient environment (90-95% RH, 25 °C) without encapsulation, respectively.

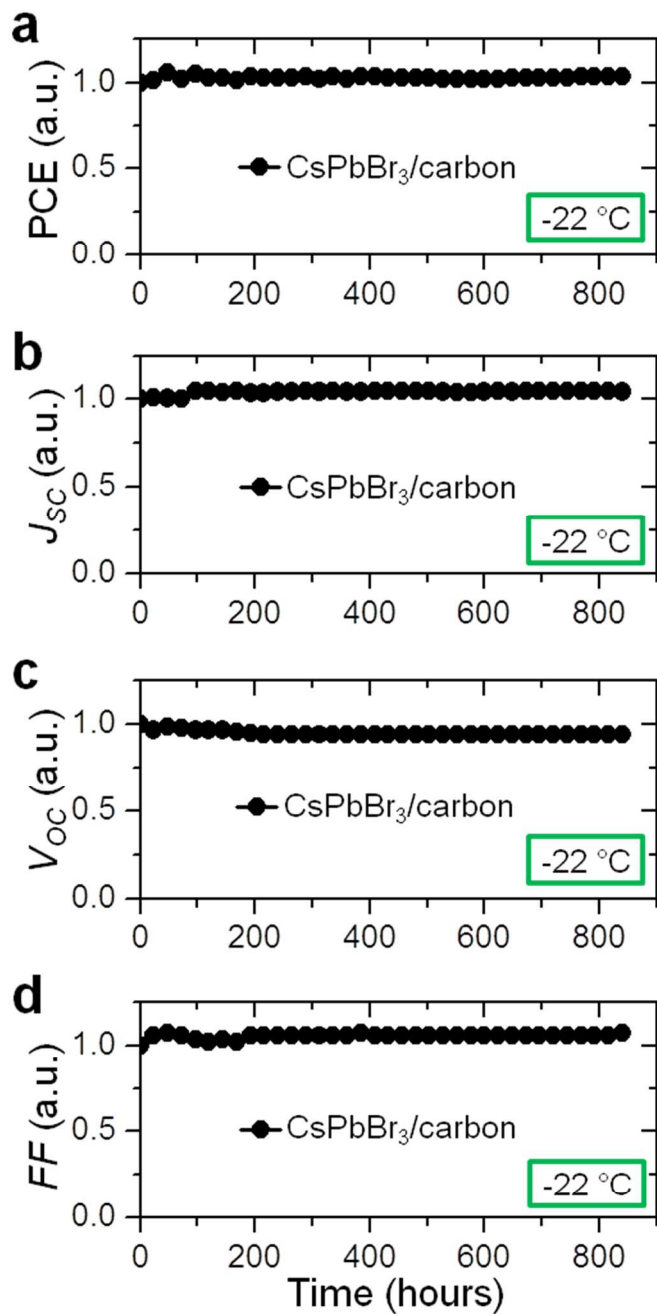


Figure S10. Stability investigations of CsPbBr₃/carbon based all-inorganic PSCs at low temperature (-22 °C) condition without encapsulation. (a) Normalized PCE, (b) J_{SC} , (c) V_{OC} and (d) FF of CsPbBr₃/carbon based all-inorganic PSCs as a function of time at low temperature (-22 °C) without encapsulation, respectively.

Table S3. Photovoltaic parameters of CsPbBr₃/carbon based all-inorganic PSCs with a large active area of 1.0 cm² measured with forward scanning mode and reverse scanning mode.

Scanning modes	J_{SC}	V_{OC}	FF	PCE
Reverse	6.96	1.26	0.57	5.0
Forward	6.99	1.26	0.51	4.5

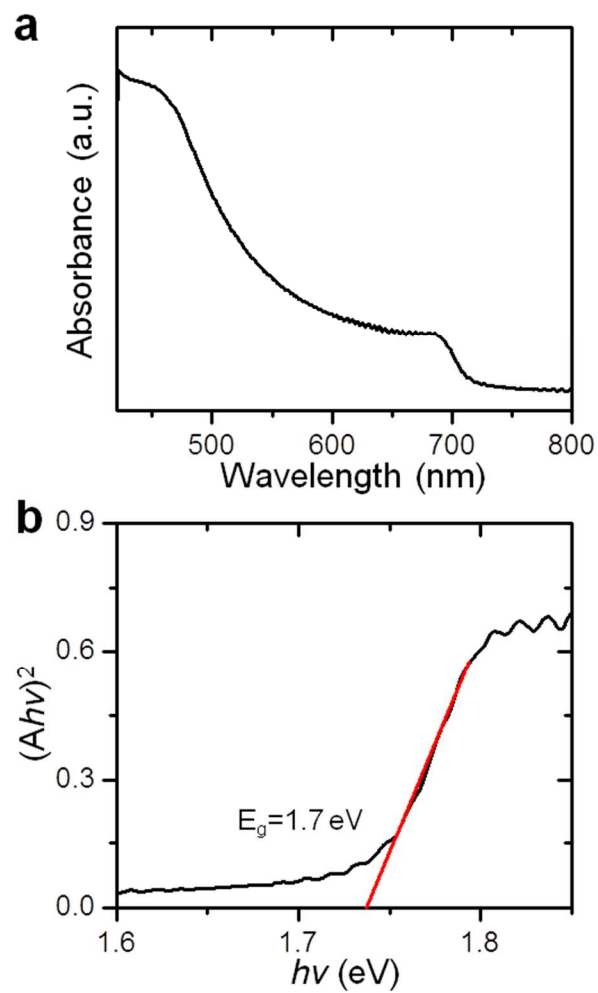


Figure S11. Absorbance spectrum and optical band gap of CsPbI₃ film. (a) Absorbance spectrum and (b) corresponding $(Ah\nu)^2$ vs. energy ($h\nu$) curve of CsPbI₃ film. The optical band gap of CsPbI₃ is measured to be ~ 1.7 eV.

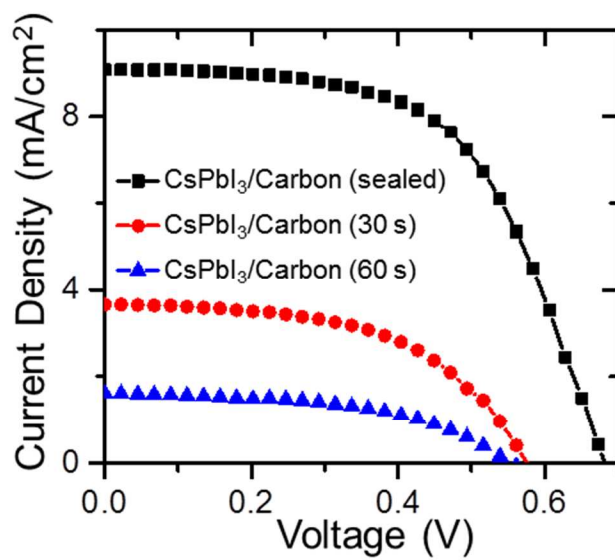


Figure S12. Photovoltaic performances of CsPbI₃/carbon based all-inorganic PSCs. *J-V* plots of sealed CsPbI₃/carbon based all-inorganic PSCs and after exposed in humid air (90-95% RH, 25 °C) without encapsulation for 30 s and 60 s, respectively.

Table S4. Photovoltaic parameters of the CsPbI₃/carbon based all-inorganic PSCs. Photovoltaic parameters of sealed CsPbI₃/carbon based all-inorganic PSCs and after exposed in humid air (90-95% RH, 25 °C) without encapsulation for 30 s and 60 s, respectively.

Aging Time	J_{SC} (mA/cm ²)	V_{OC} (V)	FF	η (%)
CsPbI ₃ /carbon (sealed)	9.08	0.70	0.57	3.60
CsPbI ₃ /carbon (30 s)	3.66	0.58	0.53	1.13
CsPbI ₃ /carbon (60 s)	1.61	0.56	0.50	0.45

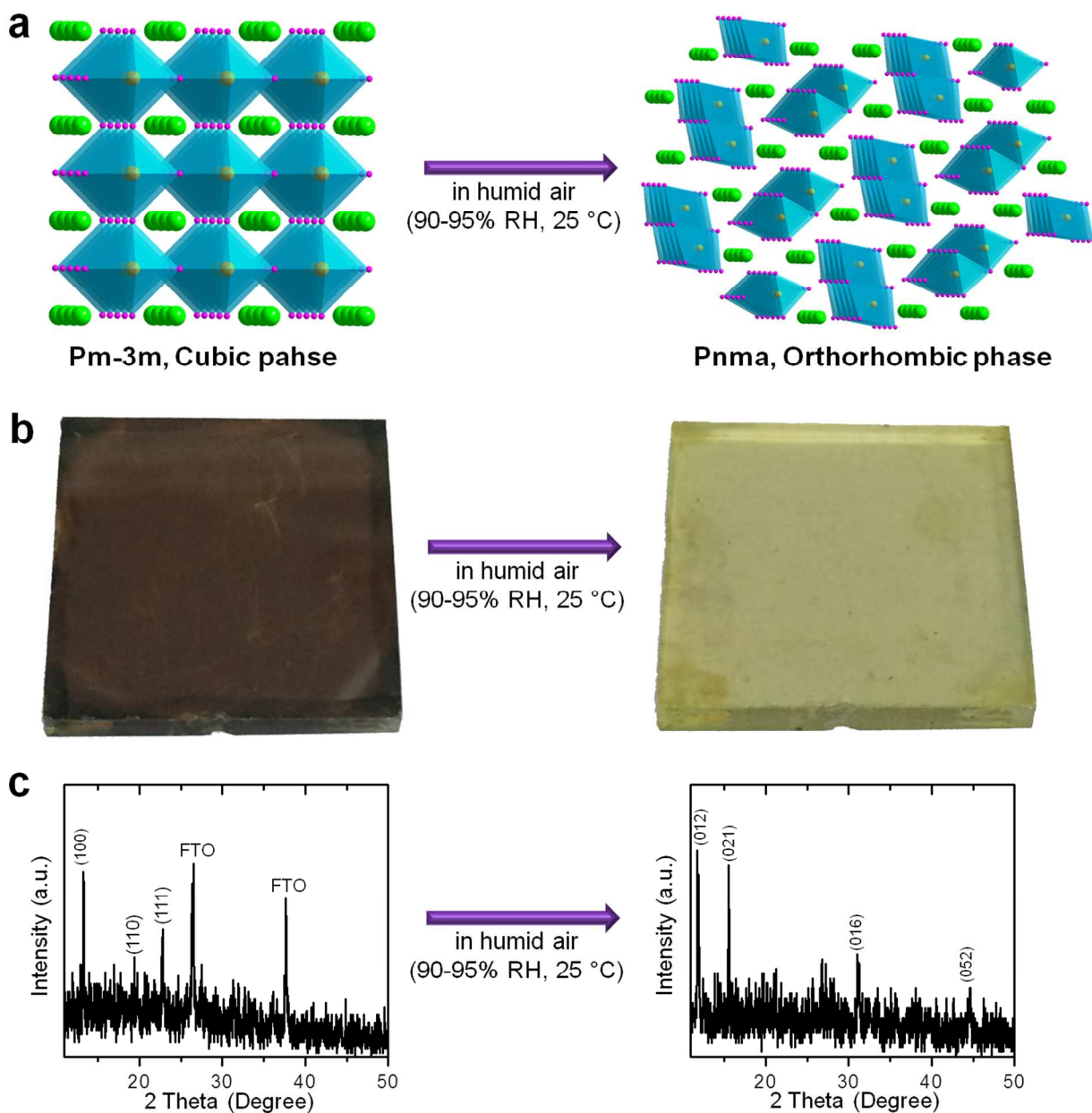


Figure S13. Crystal structure transformation and color change of CsPbI₃ in humid air. (a) The crystal structure of CsPbI₃ would rapidly transfer from perovskite cubic phase to non-perovskite orthorhombic phase in humid air (90-95% RH, 25 °C). (b) The color of CsPbI₃ film would rapidly change from dark brown to yellow in 2-3 min in humid air (90-95% RH, 25 °C). (c) XRD characterizations of the CsPbI₃ film before and after the crystal structure transformation, indicating the phase transformation from perovskite cubic phase to non-perovskite orthorhombic phase (The peaks marked by “FTO” represent the XRD peaks of FTO).