Supporting information

Enhanced performance of BiI_3-incorporated $CsPbBr_3$ solar cells

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Section 1 Experimental

Materials

All chemicals and reagents are used as is without further purification. Anhydrous dimethyl sulfoxide (DMSO), anhydrous N, N-dimethylformamide (DMF) and bismuth iodide (BiI_3) were purchased from Beijing InnoChem Technology Co., Ltd. Lead bromide ($PbBr_2$) was purchased from Aladdin Reagent (Shanghai) Co., Ltd. Cesium bromide (CsBr), stannous chloride dihydrate ($SnCl_2•H_2O$) and thiourea ($C(NH_2)_2S$) were purchased from Alfa Aesar (China) Chemical Co., Ltd. FTO glass (1.5 cm × 1.5 cm, 8 Ω) and conductive carbon paste were purchased from Shanghai Zaofu Lead Bromide New Material Co., Ltd. Anhydrous ethanol was purchased from Macklin.

Preparation of precursor solution

1.835 g of $PbBr_2$ was weighed into a sample bottle, then 5 mL of dimethylformamide (DMF) solution was added and heated at 100°C on a heating table to dissolve $PbBr_2$ precursor solution. Weigh 1.491 g of CsBr into a 100 mL volumetric flask, add 100 mL of methanol solution to the flask and dissolve by sonication to obtain the CsBr precursor solution.

Preparation of BiI_3 incorporated $CsPbBr_3$ films

The surface of the FTO glass substrate was irradiated with ultraviolet ozone cleaner for 30 min, and the $PbBr_2$ solution and FTO glass were preheated at 100℃ on the heating table, and then 80 μL $PbBr_2$ solution was measured with a pipette gun and applied on the FTO while hot, and then the FTO was heated at 100℃ for 30 min. After heating, the substrate is brought to room temperature to obtain a white $PbBr_2$ film. The 80 μL CsBr solution was spin-coated onto the $PbBr_2$ film, heated at 250 ° C for 5 min, and then cooled to room temperature. This process was repeated for 9 times to obtain an orange $CsPbBr_3$ film. The incorporated samples were obtained by incorporating 1 M $PbBr_2$ solution with different concentrations of BiI_3.

Solar cell device assembly

1.015 g of $SnCl_2$-$2H_2O$ and 0.335 g of thiourea were added to a beaker, dissolved in 30 ml of deionised water, stirred at room temperature for 36 hours and centrifuged at 9000 rpm for 5 minutes. The supernatant was filtered through a 0.22 μm PTFE filter to obtain a clear yellow SnO_2 solution. The FTO glass was irradiated with UV ozone cleaner for 30 minutes and the SnO_2 solution was then preheated on a heating table at 80 °C together with the FTO glass substrate. The hot SnO_2 solution was spin-coated onto the FTO substrate at 2000 r/min for 30 seconds and annealed at 200 °C for 1 hour to

obtain a dense SnO_2 layer. A $CsPbBr_3$ film was prepared on top of the SnO_2 and finally a 0.04 cm^2 carbon paste was applied to the $CsPbBr_3$ film. A complete cell unit was made by heating at 100 °C for 10 minutes.

Characterizations

The crystal structures were analysed by X-ray diffraction (XRD, New D8-Advance, Bruker-AXS). The morphology of $CsPbBr_3$ films with different BiI_3 incorporating was analysed by FEI Sirion 200 field emission scanning electron microscopy (SEM) and atomic force microscopy (AFM). For X-ray photoelectron spectroscopy (XPS) is the British Thermo Fisher K-Alpha. Absorption curves were measured by UV-Vis-NIR spectrophotometer (Cary 5000 UV-Vis, Varian). Steady-state PL and TRPL were collected by a fluorescence spectrophotometer equipped with a 465 nm excitation wavelength. TSPV signals were recorded using a 355 nm pulsed laser. Tafel curves were tested using a CHI600E electrochemical workstation. *J-V* characteristic curves were measured in air under AM1.5 sunlight generated by NEWPORT 91195A-SYS/EB-4 solar simulator.

Section 2 Figs. S1-S5 and Table S1-S2

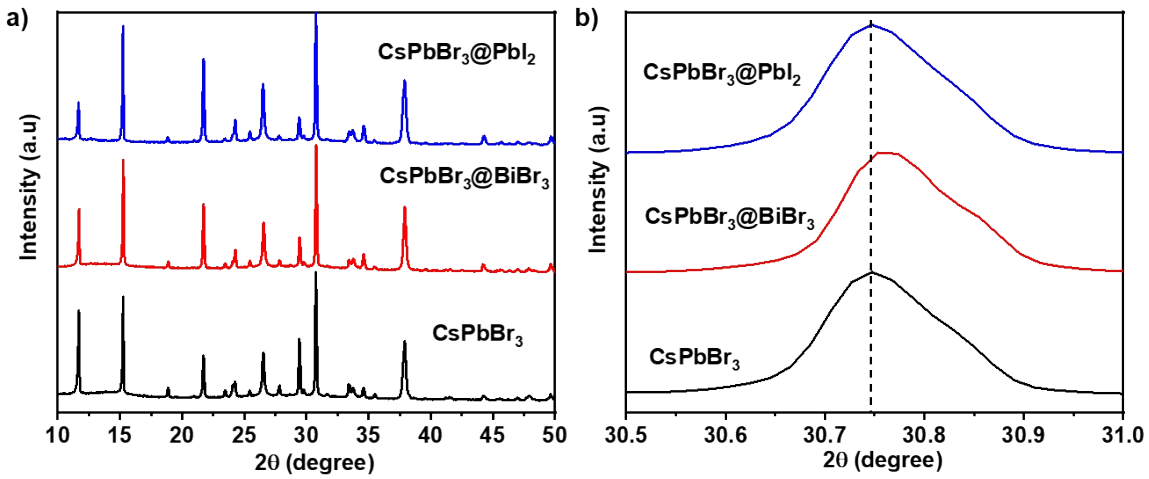

Fig. S1 (a)XRD pattern and (b) local enlargement of $CsPbBr_3$ film at 0.5% $BiBr_3$ and PbI_2 incorporating concentration

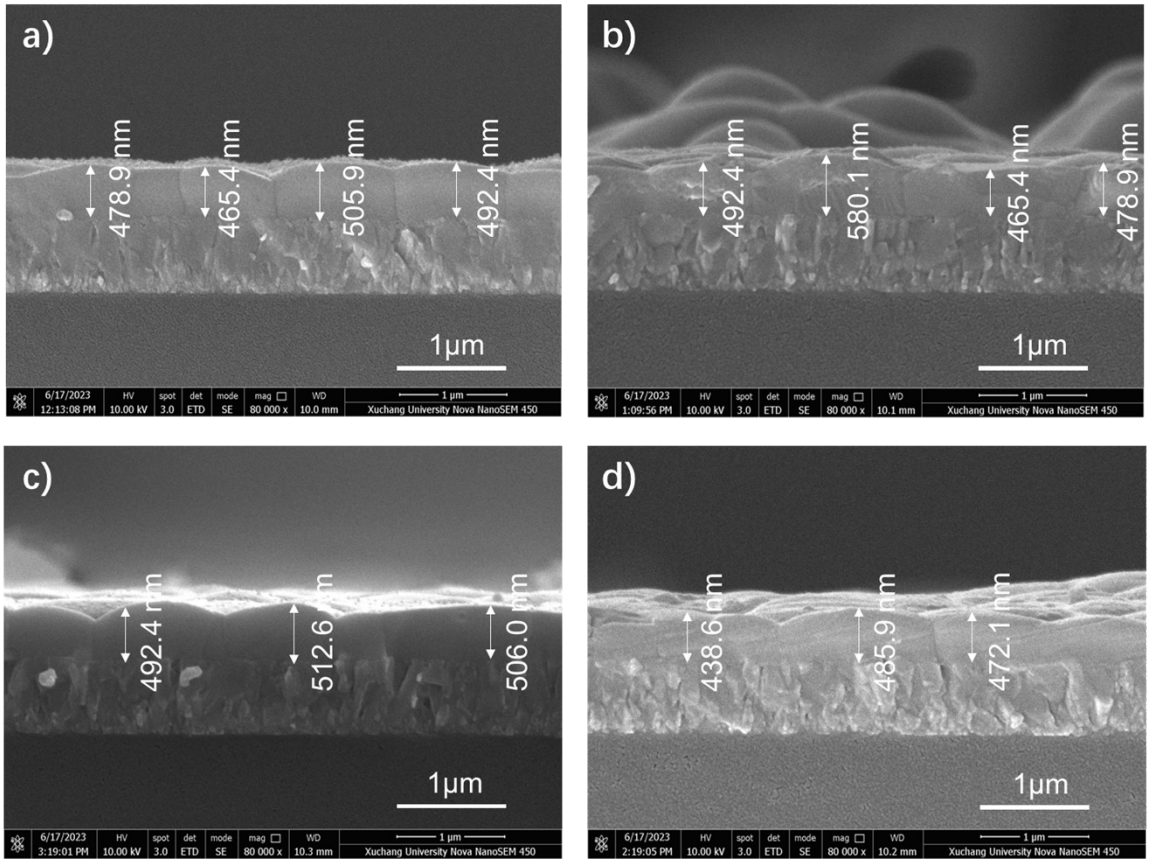

Fig. S2 SEM photographs of the cross section of $CsPbBr_3$ thin films at (a) 0.0 %, (b) 0.1 %, (c) 0.5 % and (d) 1.0 % BiI_3

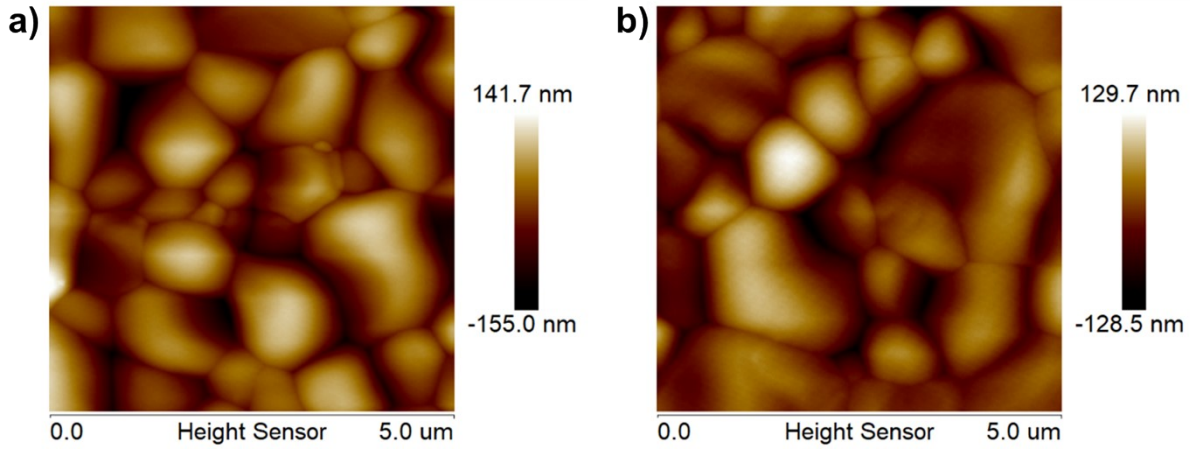

Fig. S3 AFM images of $CsPbBr_3$ films at the concentration of (a)0.0% and (b)0.5% BiI_3

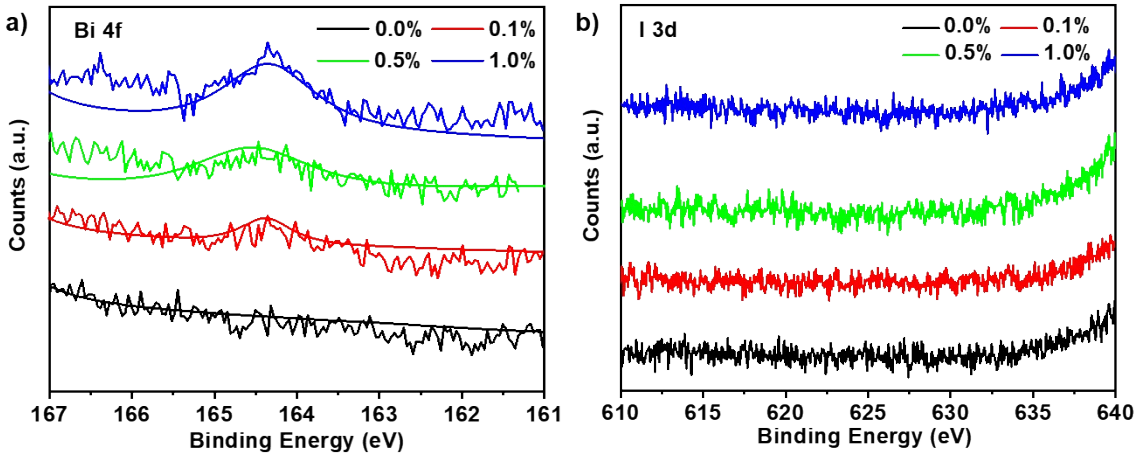

Fig. S4 XPS spectra of $CsPbBr_3$ films (a) Bi 4f and (b) I 3d at different incorporating concentrations

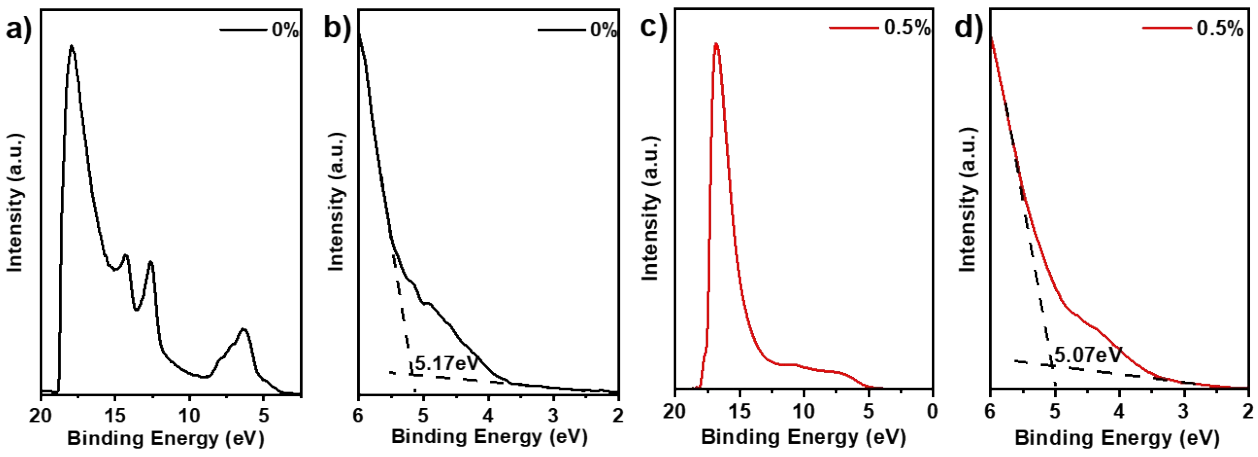

Fig. S5 UPS patterns of $CsPbBr_3$ thin films at 0.0% and 0.5% BiI_3 incorporating concentration

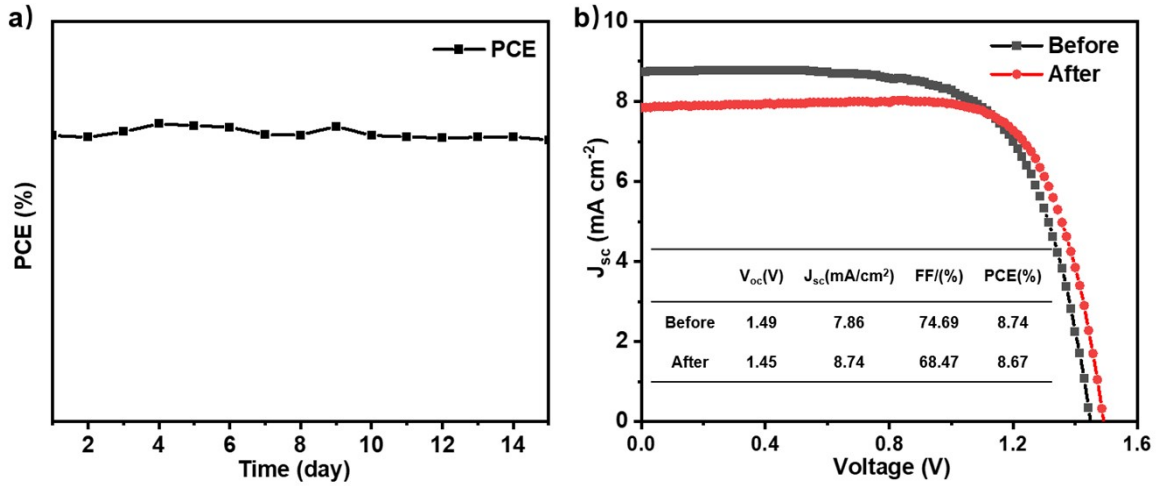

Fig. S6 The stability of the 0.5% BiI_3-incorporated $CsPbBr_3$ all-inorganic perovskite solar cells was evaluated through two sets of tests: (a) a stability test at room temperature (25 °C) and relative humidity of 35 ± 5%, and (b) a stability test after heating the cells at 100 °C for 3 hours. These tests aimed to assess the performance and reliability of the solar cells under different environmental conditions.

Table S1 EDS element content of $CsPbBr_3$ film with 0.5% BiI_3 incorporating content

Element	Line type	Apparent concentration	wt%	wt% Sigma	Atomic percent ratio
Br	L	45.15	38.53	1.29	57.55
I	L	0.38	0.34	0.93	0.32
Cs	L	23.87	21.45	1.33	19.26
Pb	M	40.09	39.46	1.52	22.73
Bi	M	0.22	0.23	1.70	0.13
Overall amount			100.00		100.00

Table S2 TSPV parameters of $CsPbBr_3$ films with different BiI_3 incorporating concentrations.

Sample	T_t (s)	T_r (s)	T_t/T_r
$CsPbBr_3$	6.5×10^{-7}	4.3×10^{-4}	1.5×10^{-3}
0.1% BiI_3-$CsPbBr_3$	6.1×10^{-7}	2.3×10^{-3}	2.6×10^{-4}
0.5% BiI_3-$CsPbBr_3$	7.4×10^{-7}	3.8×10^{-3}	1.9×10^{-4}
1.0% BiI_3-$CsPbBr_3$	7.8×10^{-7}	1.0×10^{-3}	7.8×10^{-4}

Table S3 Summary of the photovoltaic parameters of $CsPbBr_3$ PSCs with champion PCE.

Device structure	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF (%)	PCE (%)	Ref
FTO/SnO_2/0.5%BiI_3-$CsPbBr_3$/carbon	8.66	1.52	72.47	9.54	This work
FTO/TiO_2/$CsPbBr_3$/carbon	7.37	1.37	76.00	7.65	S1
FTO/TiO_2/$CsPbBr_3$/carbon	7.40	1.22	81.4	7.37	S2
FTO/SnO_2/$CsPbBr_3$/Carbon	7.64	1.52	79.00	9.14	S3
FTO/SnO_2/$CsPbBr_3$/BaI_2/Carbon	7.95	1.55	82.00	10.09	S4
FTO/TiO_2/Turmeri-$CsPbBr_3$/carbon	11.94	1.24	66.11	9.78	S5
FTO/TiO_2/Carotene-$CsPbBr_3$/carbon	8.81	1.32	67.31	7.81	S5
FTO/TiO_2/$CsPbBr_3$/$ReSe_2$/carbon	7.92	1.62	83.06	10.67	S6
FTO/TiO_2/DAP/$CsPbBr_3$/carbon	7.51	1.62	84.05	10.31	S7
FTO/SnO_2-TiO_xCl_{4-2x}/WS_2/$CsPbBr_3$/carbon	7.95	1.70	79.00	10.65	S8
FTO/SnO_2 QDs/$CsPbBr_3$/$CsSnBr_3$ QDs/carbon	7.80	1.61	84.40	10.60	S9
ITO/SnO_2/$CsPbBr_3$/Spiro-OMeTAD/Au	7.13	1.23	68.00	5.96	S10
FTO/TiO_2/$CsPbBr_3$/carbon	8.36	1.44	78.00	9.36	S11
FTO/TiO_2/ASF/$CsPbBr_3$/carbon	7.47	1.62	83.56	10.08	S12
FTO/SnO_2/$CsPbBr_3$@ECTF-1/Carbon	7.07	1.53	77.00	8.28	S13

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