Supporting Information

DOI 10.1007/s12200-017-0716-6

Hole transporting layer free inverted mixed lead-tin perovskite thin film solar cells

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Methods

Materials were obtained as follows: Triton X-100 (Sigma/VETEC, RG), deionized water (purite dispenser, >18 MΩ), ethylene glycol (Sigma-Aldrich, 99.5%), *N*,*N*-dimethylformamide (DMF) (Sigma-Aldrich, anhydrous, 99.8%), dimethyl sulfoxide (DMSO) (Sigma-Aldrich, anhydrous, 99.9%), PbI_2 (Sigma-Aldrich, 99%), tin fluoride(SnF_2) (Macklin, 99.9%), toluene (Sigma-Aldrich, HPLC, 99.9%), chlorobenzene (Sigma-Aldrich, anhydrous, 99.8%), PCBM (Nano-C, 99%), BCP (Xi'an p-OLED, 99%). Other chemicals were purchased from Sinopharm chemical reagent Co. Ltd. SnI_2 was prepared according to Ref. [1].

Formamidinium iodide ($CH(NH_2)_2I$, FAI) 9.3 mL of hydriodic acid was added to 50 mL round-bottom flask which contained 5.2 mg of formamidine acetate and then was stirred for 20 min at room temperature. The white precipitate was recovered by evaporating the reaction mixture at 90°C for 10 min. The product was dissolved in ethanol and recrystallized by ethyl acetate. After recrystallized twice, the resulting FAI was collected by filtration and dried at 60°C overnight in a vacuum oven.

NiO_x film fabrication NiO_x precursor solution was prepared according to literature [2]. Nickel (II) nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$) and ethylene diamine were dissolved in ethylene glycol solution in 1:1 molar ratio and stirred at 70°C for 3 h in oil bath to attain a 1 M precursor solution. The solution was spin-coated onto an ITO substrate at 2000 rpm for 90 s and then annealed at 300°C for 1 h in a muffle furnace. All the NiO_x substrates were treated in an UVO machine for 3 min before transferred into the glovebox for perovskite film fabrication.

Film characterizations were carried out in ambient environment unless otherwise stated. X-ray diffraction (XRD) was performed with a Bruker D8 Advance powder diffractometer using Cu $K\alpha_{1/2}$ source in θ-θ model. Photoluminescence (PL) spectra were recorded by exciting the perovskite films at 650 nm with a standard 450-W Xenon CW lamp. The signal was recorded with a spectrofluorometer (Fluorolog; HORIBA FL-3) and analyzed with the software Fluor Essence. The absorption (Abs) spectra of the perovskite films were measured by *UV-vis* spectrophotometer (Agilent cary5000). The measurements were carried out in air condition with temperature of (18 ± 1)ºC, and humidity of (40 ± 2)% RH. Films were imaged with a high-resolution

field emission scanning electron microscope (SEM) (Carl Zeiss Microscopy GmbH Supra 55) and exposed to air for a short time while being transferred to the vacuum chamber.

X-ray photoelectron spectroscopy (XPS) was performed for films on ITO substrates using a Thermo ESCA 250XI. Films were unavoidably exposed to air during the preparation process for approximately 1 min. XPS measurements were carried out in a vacuum system with a base pressure of 5×10^{-10} mbar. The samples were etched with a beam of 0.5 keV Ar^{+} ions for 15 s. Curve fitting was performed using the Thermo Avantage software. Given the possible drift of the spectra, the curves were corrected based on the C_{1s} peak at 284.8 eV.

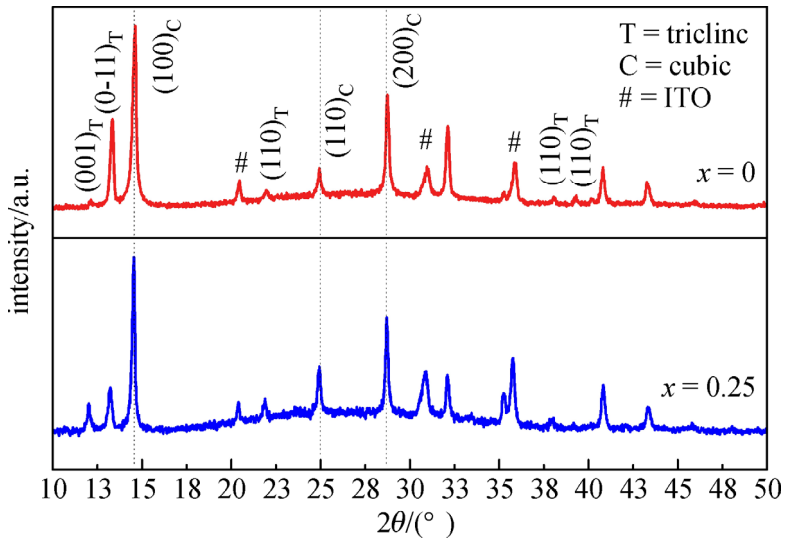

Fig. S1 X-ray diffraction patterns of $FAPb_{1-x}Sn_xI_3$ films (x=0 and 0.25), and the peaks corresponding to triclinic and cubic structure

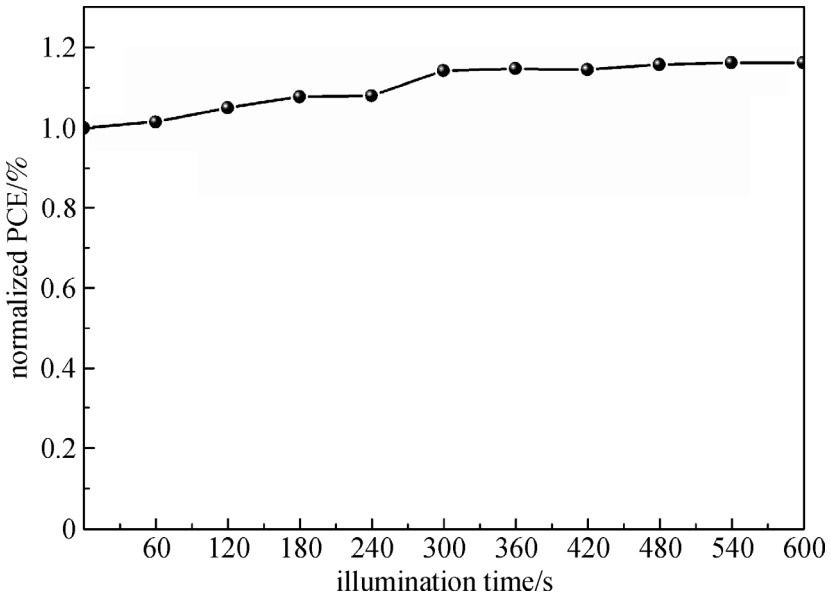

Fig. S2 PCE of the device under continuous simulated AM 1.5 illumination

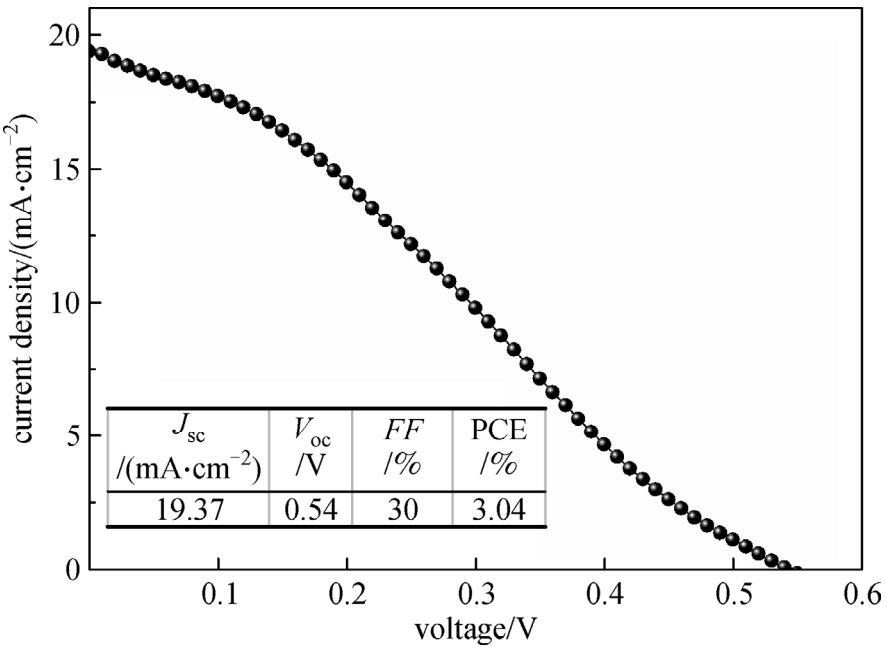

Fig. S3 Representative *J-V* characteristics of the ITO/NiO_x/$FAPb_{0.5}Sn_{0.5}I_3$/PCBM/BCP/Al device

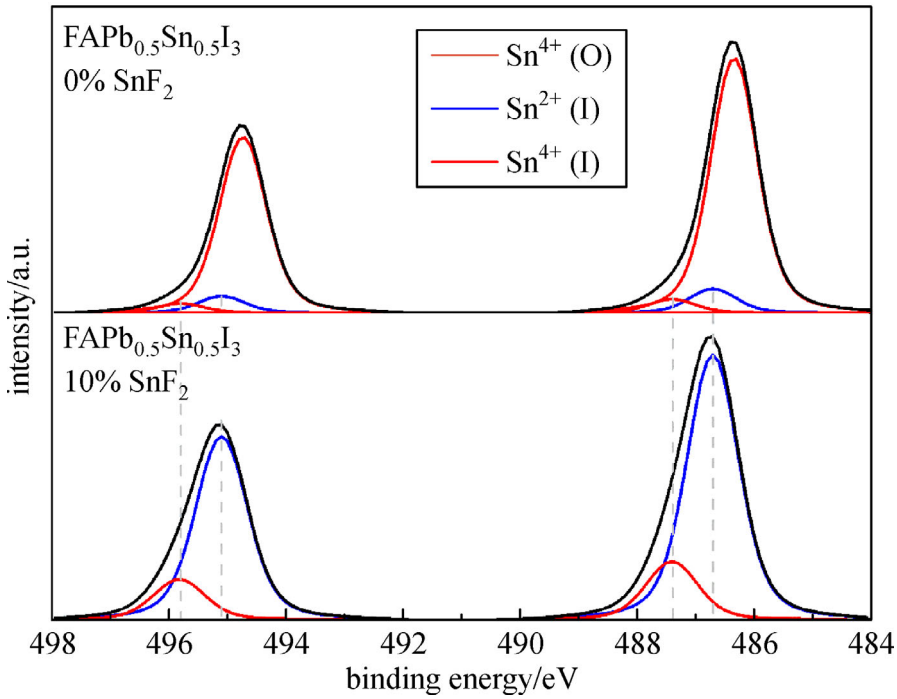

Fig. S4 XPS Sn *3d* spectra (black) of $FAPb_{0.5}Sn_{0.5}I_3$ films without SnF_2 and with 10 mol% SnF_2 with a 15 s etching time. The two peaks deconvoluted from the spectra at 486.7 and 487.4 eV are associated with Sn^{2+} (blue) and Sn^{4+} (red) cooperating with iodide, respectively. Peak at 486.3 eV are related to the Sn^{4+} (orange) cooperating with oxygen

Table S1 Sn^{4+} and Sn^{2+} contents (%) in $FAPb_{0.5}Sn_{0.5}I_3$ films with different SnF_2 concentration

SnF_2 content	Sn^{4+}- O/%	Sn^{4+}- I/%	Sn^{2+}- I/%
0%	87.03	4.71	8.26
10%	/	17.94	82.06

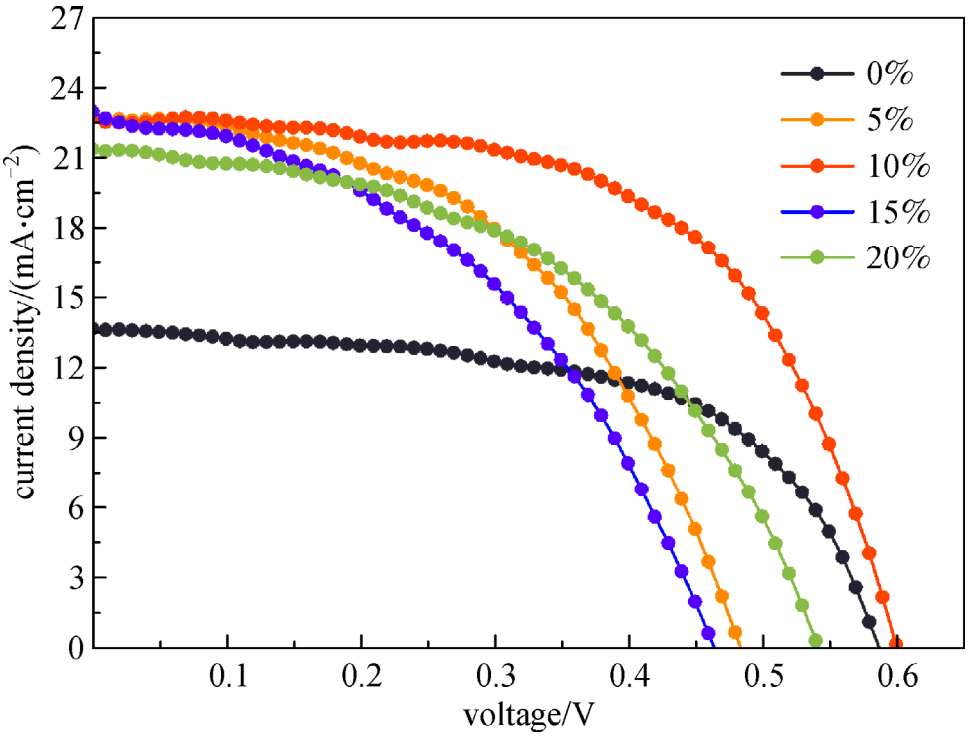

Fig. S5 Representative *J-V* characteristics of ITO/ $FAPb_{0.5}Sn_{0.5}I_3$/PCBM/BCP/Al devices with varying SnF_2 content

Table S2 Photovoltaic performances for $FAPb_{0.5}Sn_{0.5}I_3$ with different SnF_2 content

SnF_2 content	J_{sc} /(mA·cm^{-2})	V_{oc} /V	*FF* /%	PCE /%	R_s /Ω	R_{sh} /Ω
0%	13.64	0.59	58	4.70	208	10581
5%	22.84	0.48	49	5.40	171	3083
10%	23.13	0.59	58	7.94	151	20017
15%	22.95	0.46	44	4.66	195	1226
20%	21.87	0.55	48	5.77	199	25571

References

1. Yokoyama, T.; Cao, D. Y. H.; Stoumpos, C. C.; Song, T. B.; Sato, Y.; Aramaki, S.; Kanatzidis, M. G. Overcoming Short-Circuit in Lead-Free $CH_3NH_3SnI_3$ Perovskite Solar Cells via Kinetically Controlled Gas-Solid Reaction Film Fabrication Process. *J Phys Chem Lett* **2016,** 7(5), 776-782.

2. Quan, L. N.; Yuan, M.; Comin, R.; Voznyy, O.; Beauregard, E. M.; Hoogland, S.; Buin, A.; Kirmani, A. R.; Zhao, K.; Amassian, A.; Kim, D. H.; Sargent, E. H. Ligand-Stabilized Reduced-Dimensionality Perovskites. *J. Am. Chem. Soc.* **2016,** 138 (8), 2649-2655.