Electronic Supplementary Information (ESI)

Highly efficient and stable air-processed hole-transport-material free carbon based perovskite solar cells with caesium incorporation

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Experimental section:

1. Materials

PbI_2 (TCI, 99.99%), MAI (MACKLIN, 99.5%), FAI (MACKLIN, 99.5%), CsI (Energy Chemical, 99%), $Pb(SCN)_2$ (Alfa Aesar, 99.99%), DMF (Aladdin, 99.8%) and DMSO (Aladdin, 99.8%) were employed directly without any treatment.

2. $Cs_X(MA_{0.7}FA_{0.3})_{1-X}PbI_3$ perovskite precursors

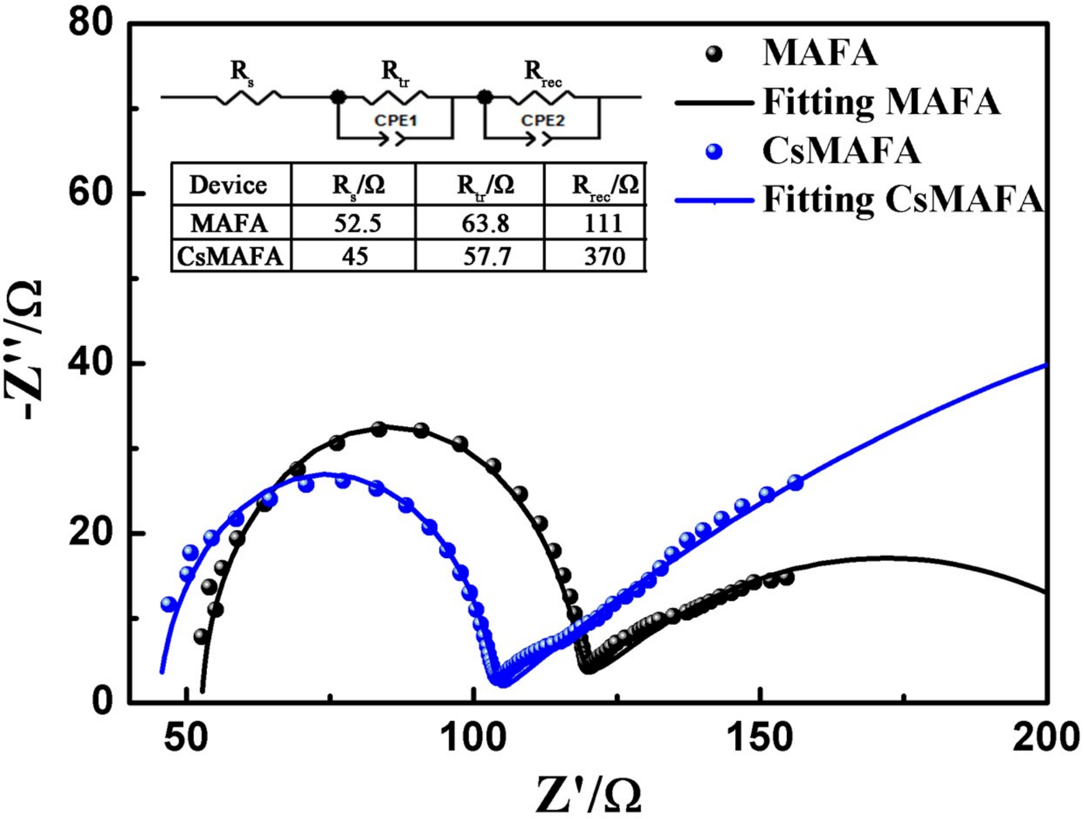
$Cs_X(MA_{0.7}FA_{0.3})_{1-X}PbI_3$ precursors were prepared by mixing $MA_{0.7}FA_{0.3}PbI_3$ and $CsPbI_3$ precursors with different volume ratios and stirred at 65℃ for at least one hour before using 1M $MA_{0.7}FA_{0.3}PbI_3$ precursor was prepared by the dissolution of 461 mg PbI_2, 51.6 mg FAI and 111.3 mg MAI with 9.22 mg $Pb(SCN)_2$ additive in DMF/DMSO (volume ratio=4:1) mixed solvents. 1M $CsPbI_3$ precursor was prepared by dissolving 461 mg PbI_2 and 259.8 mg CsI in DMF/DMSO (volume ratio=7:3) mixed solvents.

3. Device Fabrication

The perovskite solar cells (PSCs) were fabricated with a structure of FTO/bl-TiO_2/mp-TiO_2/Perovskite/Carbon. The device fabrication process can be referred in our previous works except for the perovskite layer.[1-3] In brief, $(MA_{0.7}FA_{0.3}PbI_3)_{1-X}(CsPbI_3)_X$ was deposited onto the electronic transport layer (ETL) by a one-step method. The perovskite precursor solution was spin-coated in two-step program at 1000 rpm and 4000 rpm for 5 s and 60 s respectively. Then chlorobenzene as the anti-solvent approach was poured onto the film at 5 s of the second step. After that, the as-prepared perovskite films were annealed at 100℃ for 10 min. All procedures above were completed under ambient environment with ～50% relative humidity.

4. Characterization

The surface morphologies of perovskite films were characterized with scanning electron microscopy (SEM, S-4800, Hitach, Japan). Absorbance spectra was detected by UV-vis spectrometer (Lambda 650S, PerkinElmer). The perovskite crystal structure was measured by an X-ray diffraction spectrometer (XRD, D8 Advance, Bruker AXS, Germany) with Cu Kα radiation. The current density-voltage curves were recorded on a sunlight simulator (Newport, 91192) under one sun illumination (AM 1.5G, 100 mV cm^{-2}). the J-V curves presented in the main text are obtained with a reverse scan direction from +1.1 V to -0.1 V with a scan rate of 0.05 v s^{-1}.Every *J-V* curve contains 1200 data points with a sample interval of 0.001 V, and the dwell time is 2 seconds. The element distribution was obtained by X-ray photoelectron spectroscopy (XPS, ESCALAB 250XL, Thermo Fisher, USA) with Al Kα radiation of 1486.6 eV as the excitation source. The external quantum efficiency spectra was performed from 300 nm to 900 nm with a 300 W xenon lamp.



Device	R_s/Ω	R_{tr}/Ω	R_{rec}/Ω
MAFA	52.5	63.8	111
CsMAFA	45	57.7	370

Fig. S1 Impedance spectra of MAFA and CsMAFA based devices

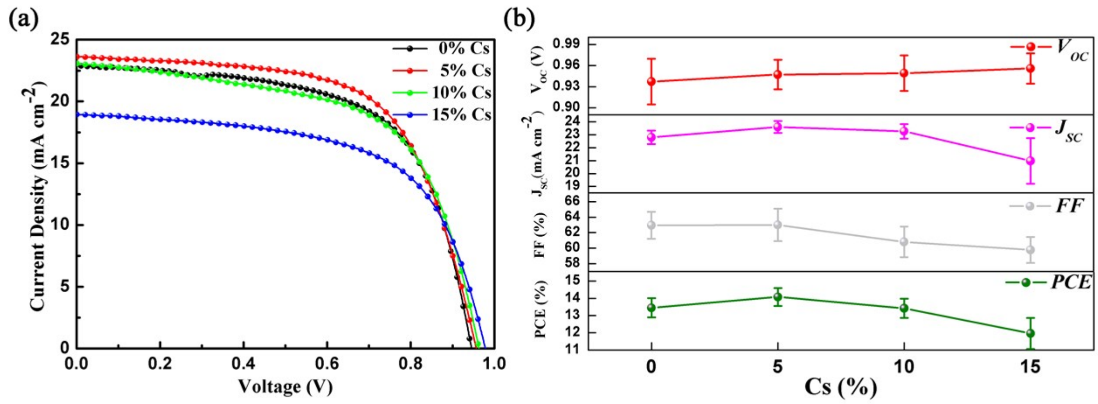


Fig. S2 Photovoltaic experiments of $Cs_X(MA_{0.7}FA_{0.3})_{1-X}PbI_3$ based devices with x varying from 0 to 15%. (a) *J-V* curves and (b) Statistical results of V_{OC}, short circuit current density (J_{SC}), fill factor (FF) and PCE of $Cs_X(MA_{0.7}FA_{0.3})_{1-X}PbI_3$ based devices.

Table S1 Parameters of V_{OC}, J_{SC}, FF and PCE of $Cs_X(MA_{0.7}FA_{0.3})_{1-X}PbI_3$ based devices. Statistical results were obtained by calculation of 30 devices for each concentration of Cs in perovskite precursor, and the error represents the standard deviation.

Device	V_{OC}(mV)	J_{SC}(mA cm^{-2})	PCE(%)	FF(%)
0% Cs	937±32	22.80±0.52	13.45±0.56	62.95±1.72
5% Cs	947±21	23.61±0.46	14.08±0.51	63.00±2.90
10% Cs	949±25	23.27±0.56	13.42±0.56	60.80±1.98
15% Cs	956±21	20.98±1.77	11.97±0.90	59.77±1.67

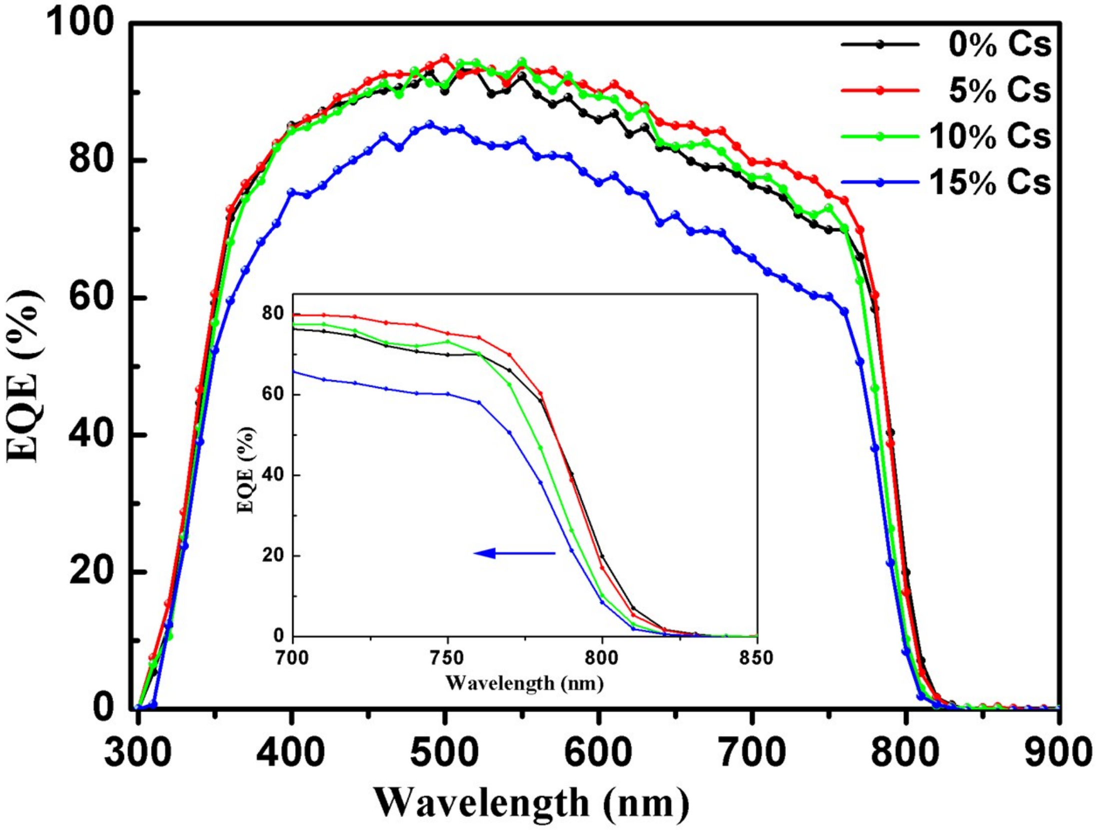
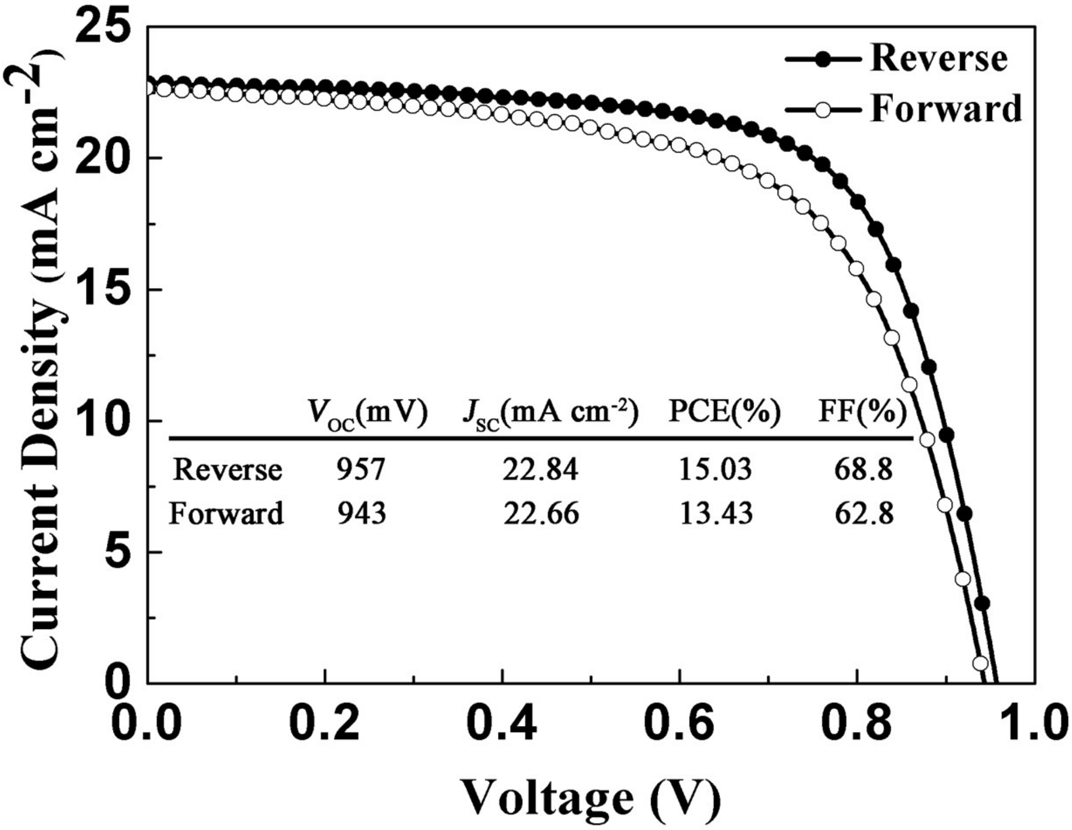


Fig. S3 the EQE curves of $Cs_X(MA_{0.7}FA_{0.3})_{1-X}PbI_3$ based devices.



	V_{OC}(mV)	J_{SC}(mA cm^{-2})	PCE(%)	FF(%)
Reverse	957	22.84	15.03	68.8
Forward	943	22.66	13.43	62.8

Fig. S4 *J*–*V* curves measured under reverse and forward voltage scans with a scan rate of 50 mV s^{-1}.

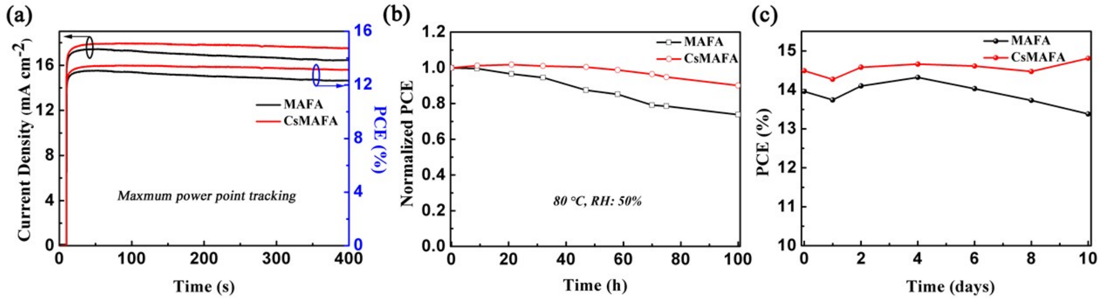


Fig. S5 Comparison of stabilities between MAFA and CsMAFA based devices. (a) Steady-state photocurrent and PCE at the maximum power point with a voltage of 0.75 V under one sun illumination, (b) Thermal stability of devices aged under a temperature of 80 °C and humidity about 50%, (c) Long-term stability of devices stored in ambient air with relatively humidity about 50% of at room temperature.

References for supporting information:

1. Y. Xiao, N. Cheng, K. K. Kondamareddy, C. Wang, P. Liu, S. Guo and X.-Z. Zhao, *J Power Sources*, 2017, **342**, 489-494.
2. Z. Yu, B. Chen, P. Liu, C. Wang, C. Bu, N. Cheng, S. Bai, Y. Yan and X. Zhao, *Adv. Funct. Mater.*, 2016, **26**, 4866-4873.
3. P. Liu, Z. Yu, N. Cheng, C. Wang, Y. Gong, S. Bai and X.-Z. Zhao, *Electrochim Acta*, 2016, **213**, 83-88.