Supporting Information

Superior stability for perovskite solar cells with 20% efficiency using vacuum co-evaporation

Xuejie Zhu,[a] Dong Yang,[a*] Ruixia Yang,[b] Bin Yang,[b] Zhou Yang,[a] Xiaodong Ren,[a] Jian Zhang,[c] Jinzhi Niu,[a] Jiamgshan Fen[a] and Shengzhong (Frank) Liu[a,b*]

[a]*Key Laboratory of Applied Surface and Colloid Chemistry, National Ministry of Education; Shaanxi Key Laboratory for Advanced Energy Devices; Shaanxi Engineering Lab for Advanced Energy Technology, School of Materials Science and Engineering, Shaanxi Normal University, Xi'an 710119, China. E-mail: dongyang@snnu.edu.cn; szliu@dicp.ac.cn*

[b]*State Key Laboratory of Molecule Reaction Dynamics, Dalian National Laboratory for Clean Energy; iChEM, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, 116023, China.*

[c]*School of Material Science and Engineering, Guangxi Key Laboratory of Information Materials, Guilin University of Electrical Technology, Guilin 541004, China.*

[d]*Center for Energy Harvesting Materials and System (CEHMS), Virginia Tech, Blacksburg, Virginia 24061, United States.*

Materials

MAI was synthesized according to a previous reported.[1] Methylamine (24 mL, 33 wt.% in absolute ethanol, Aldrich) and hydroiodic acid (10 mL, 57 wt.% in water, Aldrich) were added into 3-neck round bottom flask for 2 hour with stirring under 0 °C. The flowing nitrogen was bubbled into solution during reaction. The product was obtained by removing the solvents at 45 °C using a rotary evaporator. Re-dissolve the precipitate in just enough absolute ethanol, and add appropriate amount of diethyl ether to recrystallization. After extraction filtration, the above steps were repeated for three times to harvest pure MAI material. Finally, the product was dried at 60 °C in a vacuum oven for 24 hour. $PbCl_2$ (purity > 99.99%) and CsCl (purity > 99.99%) were purchased from Alfa-Aesar. Spiro-OMeTAD was purchased from Yingkou optimization technology co., LTD. All of the solvents were purchased from Sigma-Aldrich and used without any purification.

The ratio of Cs and Pb calculation

The ratio of Cs and Pb within perovskite films was calculated by XPS (Fig. 1a and Fig. S2) as following Eq (4):[2]

$$\frac{n_i}{n_j} = \frac{I_i}{I_j} \times \frac{\sigma_j}{\sigma_i} \times \frac{E_{kj}^{0.5}}{E_{ki}^{0.5}} \qquad (4)$$

where n is the atomic number, I is peak area of element, σ is the photoionization cross-sections of elements,[3] and E_k is photoelectron kinetic energy. The ratios of Cs and Pb are 0.11, 0.17, 0.23 and 0.34 when the deposition rates of CsCl are 0.3, 0.45, 0.6 and 0.9 Å s^{-1}, respectively.

Trap-state density measurement

The devices with structure of FTO/PEDOT:PSS/perovskite/spiro-OMeTAD/Au were fabricated to test the trap-state density in the perovskite films. Fig. S6 shows the *I-V* curves of the devices with pristine and Cs-substituted perovskite. The trap-filled limit voltage (V_{TFL}) is obtained from *I-V* plot. The trap-state density is calculated using following Eq (5):[4]

$$V_{TFL} = \frac{e n_t d^2}{2\varepsilon_0 \varepsilon_r} \qquad (5)$$

Where e is the elementary charge, d is the thickness of the perovskite film, ε_0 is the vacuum permittivity, ε_r is the relative dielectric constant of $MAPbI_3$, and n_t is the trap-state density. The V_{TFL} of the pristine and Cs-substituted $MAPbI_3$ films are 1.03 and 0.28 V, respectively. Therefore, the trap-state density of pristine and Cs-substituted $MAPbI_3$ are 1.16×10^{16} and 3.15×10^{15} cm^{-3}, respectively.

References

1. C. C. Stoumpos, C. D. Malliakas and M. G. Kanatzidis, *Inorg. Chem.*, 2013, **52**, 9019.

2. Y. Boudevilie, F. Figueras, M. Forissier, J.-L. Portefaix and J. C. Vedrine, *J. Catal.*, 1979, **58**, 52.

3. J. H. Scofield, *J. Elec. Spec.*, 1976, **8**, 129.

4. H. B. Richard, *J. Appl. Phys.*, 1962, **33**, 1733.

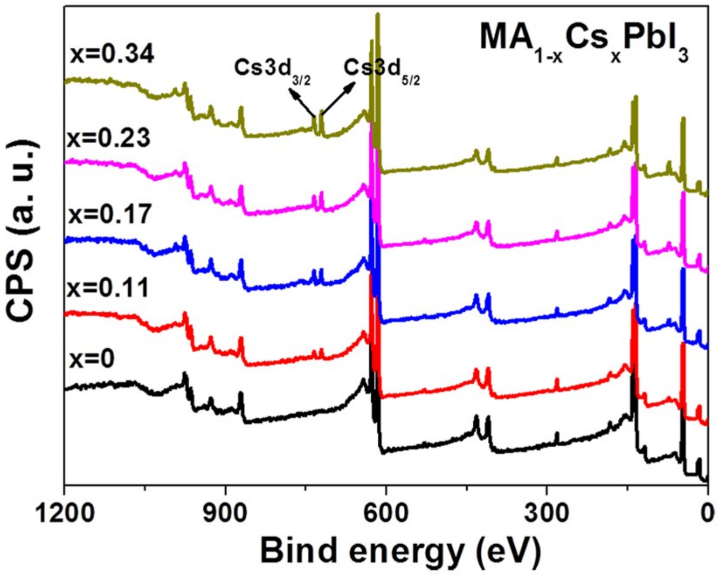

Fig. S1. The perovskite films without and with different Cs content are performed on XPS. The new peaks in Cs-substituted $MAPbI_3$ film emerge at around 730 eV, corresponding to Cs3d.

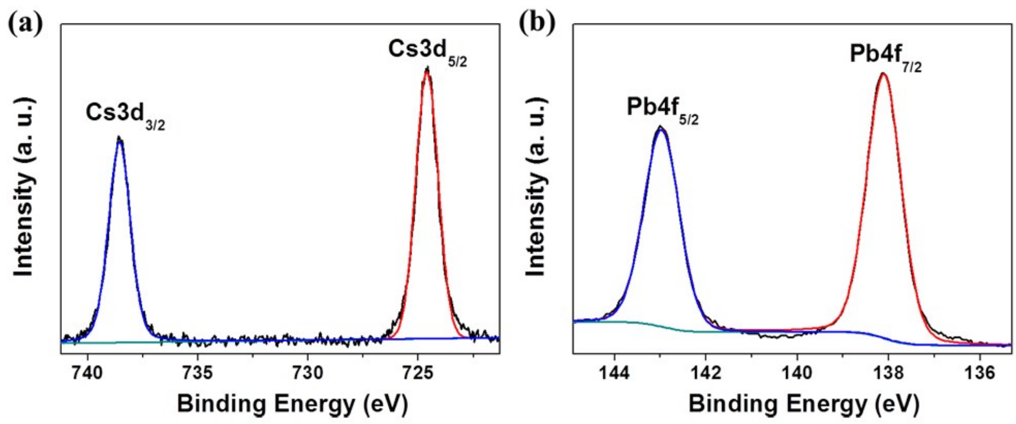

Fig. S2. XPS focus on (a) Cs3d and (b) Pb4f in perovskite films.

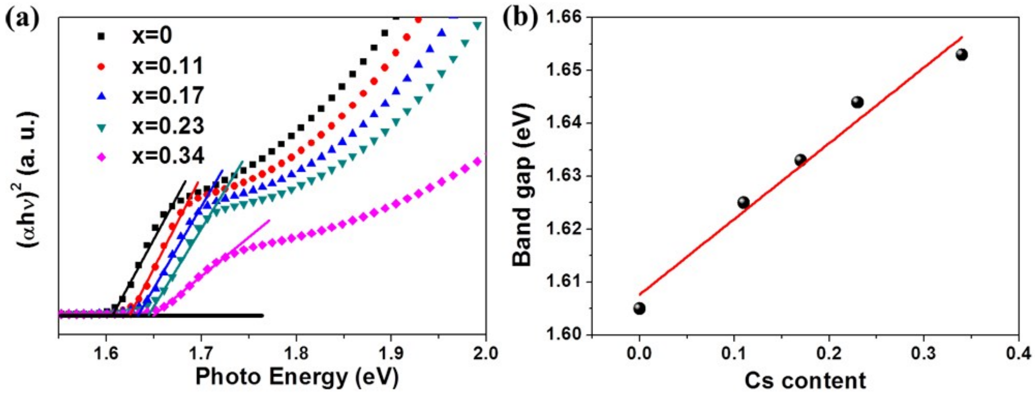

Fig. S3. (a) The band gap of $MAPbI_3$ with different Cs content. (b) The linear relationship of band gap of perovskite with Cs content.

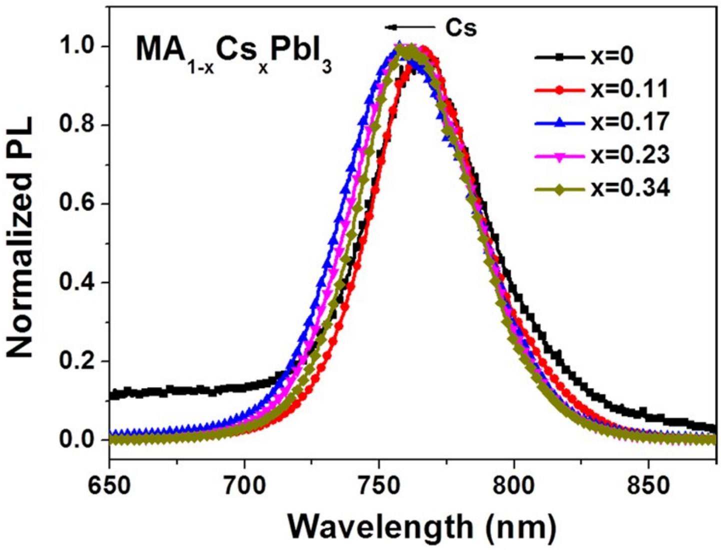

Fig. S4. The emission maximum obviously blue-shifted from 765 to 759 nm by increasing the Cs content.

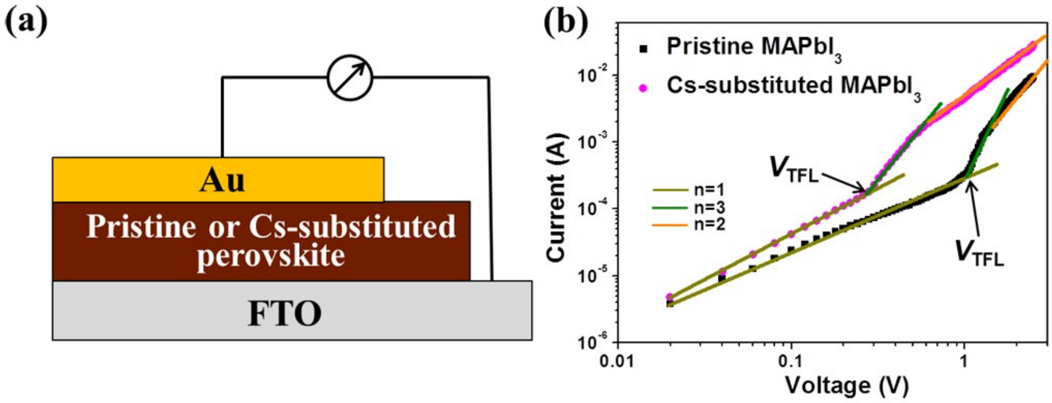

Fig. S5. (a) Device structure for trap-state density test. (b) Dark *I-V* characteristics of the $MAPbI_3$ and Cs-substituted perovskite devices revealing V_{TFL} kink point behavior. Three regions are divided by different values of the exponent n. n = 1 is the ohmic region response, n = 2 is the space charge limited current region. The current quickly increases nonlinearly when the bias voltage exceeds the kink point according to n = 3.

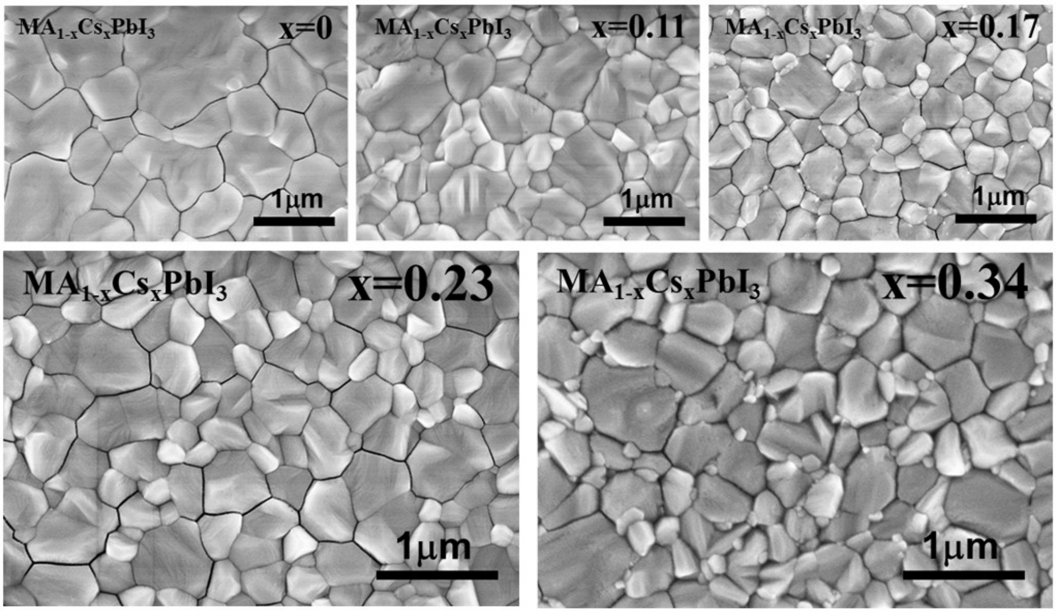

Fig. S6. Top-view SEM images of the $MAPbI_3$ perovskite films based on different Cs content.

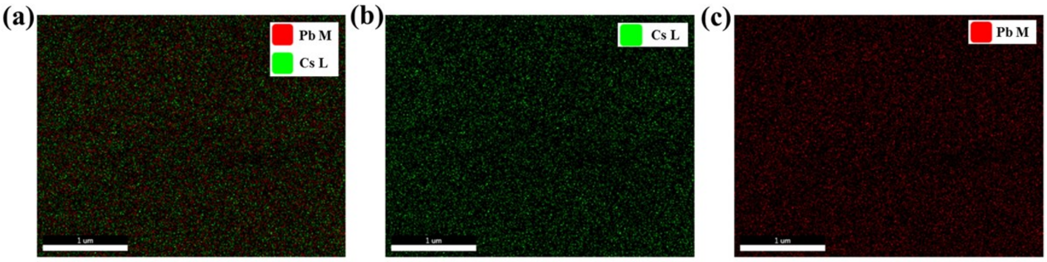

Fig. S7. (a) Pb-Cs-mapping (b) Cs-mapping (c) Pb-mapping.

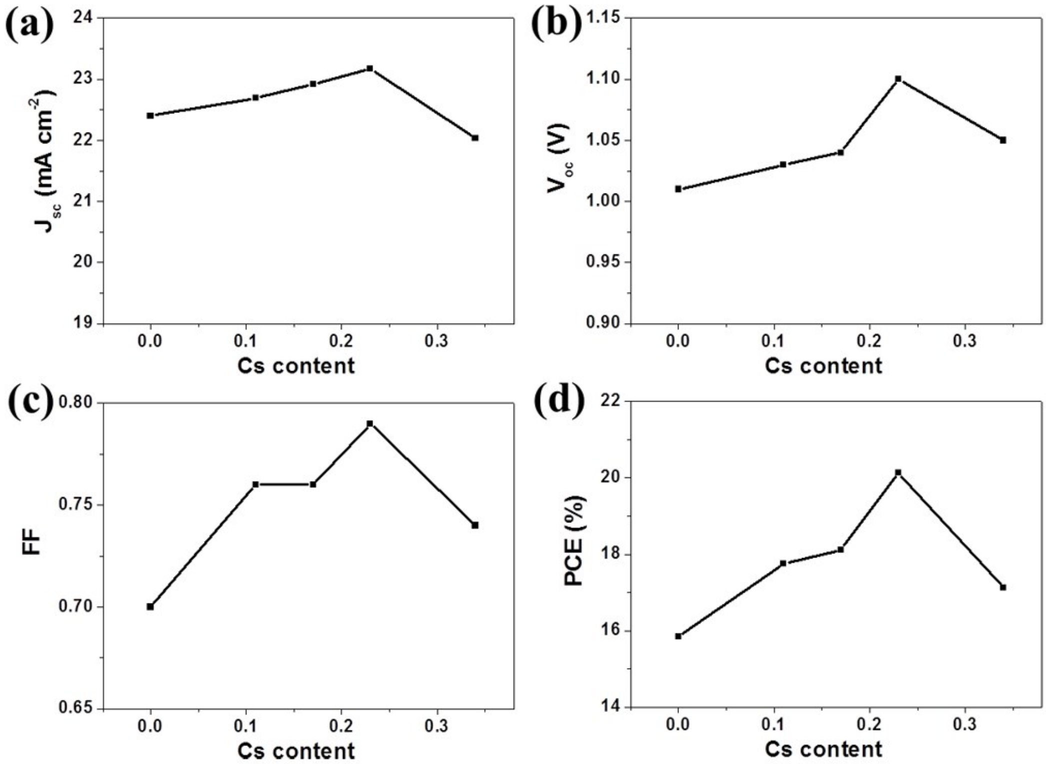

Fig. S8. The change trend of (a) J_{sc} (b) V_{oc} (c) FF and (d) PCE for PSCs when the Cs content increases from 0 to 0.34.

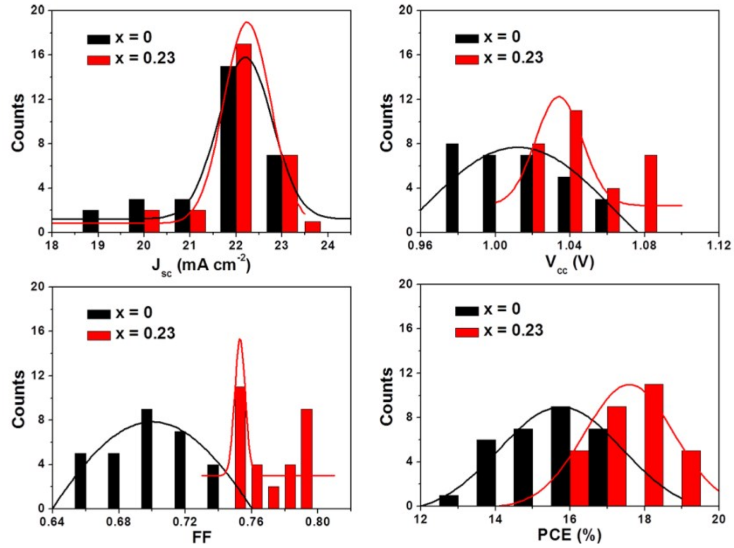

Fig. S9. The key parameters including J_{sc}, V_{oc}, FF and PCE for PSCs based on the Cs contents of 0 and 0.23.

Table S1. Parameters of the TRPL spectra based on $MA_{1-x}Cs_xPbI_3$ absorbers.

Cs content	τ_{ave} (ns)	τ_1 (ns)	τ_2 (ns)	% of τ_1	% of τ_2
0	2.83	11.96	4.67	30.24	69.76
0.11	23.13	28.56	6.12	40.02	59.98
0.17	31.71	35.82	10.05	53.44	46.56
0.23	115.35	125.31	29.73	67.10	32.90
0.34	128.85	135.18	15.06	66.76	33.24

Table S2. The parameters of PSCs based on $MAPbI_3$.

Devices	**J_{sc} (mA cm^{-2})**	**V_{oc} (V)**	**FF**	**PCE (%)**
1	22.87	0.98	0.65	14.69
2	22.39	1.02	0.70	16.03
3	22.85	1.0	0.71	16.22
4	20.18	0.98	0.72	14.25
5	22.46	1.02	0.72	16.53
6	20.72	0.98	0.72	14.78
7	23.16	1.04	0.73	17.60
8	23.13	1.04	0.73	16.94
9	22.50	1.02	0.73	16.91
10	22.65	1.02	0.74	17.14
11	22.48	1.04	0.74	17.41
12	22.76	1.02	0.75	17.33
13	20.82	0.98	0.75	15.31
14	22.68	0.98	0.76	16.90

15	23.21	1.04	0.70	16.92
16	18.37	0.98	0.73	13.14
17	22.58	1.0	0.71	15.99
18	23.04	1.06	0.66	16.13
19	22.65	1.06	0.65	15.66
20	22.02	1.0	0.67	14.73
21	21.04	1.0	0.68	14.38
22	21.62	1.0	0.69	14.96
23	21.10	0.98	0.70	14.59
24	19.34	0.98	0.75	14.20
25	22.85	1.02	0.67	15.57
26	23.54	1.06	0.69	17.31
27	22.76	1.02	0.69	16.11
28	23.09	1.0	0.66	14.64
29	22.40	1.0	0.66	14.89
30	23.75	1.04	0.70	17.27
Average	22.17±1.23	1.01±0.03	0.70±0.03	15.82±1.19

Table S3. The parameters of PSCs based on $MA_{0.77}Cs_{0.23}PbI_3$.

Devices	**J_{sc} (mA/cm^2)**	**V_{oc} (V)**	**FF**	**PCE (%)**
1	22.69	1.08	0.75	18.31
2	23.31	1.04	0.79	19.25

3	23.7	1.04	0.79	19.35
4	22.8	1.02	0.77	17.91
5	22.5	1.02	0.78	17.83
6	23.46	1	0.79	18.58
7	23.17	1.04	0.79	19.11
8	22.75	1.04	0.79	18.62
9	23.09	1.04	0.78	18.83
10	23.24	1.04	0.79	19.02
11	23.25	1.02	0.78	18.52
12	23.12	1.02	0.78	18.47
13	22.78	1.02	0.79	18.31
14	22.81	1.02	0.79	18.40
15	22.36	1.02	0.79	17.93
16	20.8	1.04	0.74	16.03
17	20.4	1.04	0.75	15.85
18	22.82	1.04	0.74	17.63
19	22.98	1.04	0.76	18.16
20	22.24	1.02	0.75	16.99
21	22.29	1.02	0.72	16.42
22	22.37	1.04	0.72	16.73
23	21.05	1.06	0.74	16.56
24	22.03	1.06	0.75	17.44

25	22.14	1.08	0.74	17.60
26	22.08	1.08	0.75	17.86
27	22.41	1.08	0.76	18.27
28	21.08	1.08	0.76	17.23
29	22.69	1.08	0.76	18.60
30	22.91	1.08	0.77	19.00
Average	22.51±0.78	1.04±0.02	0.76±0.02	17.96±0.93

Table S4. EIS parameters for the pristine $MAPbI_3$ and $MA_{0.77}Cs_{0.23}PbI_3$ devices.

Cs content	R_s (Ω)	R_{rec} (Ω)	C_{rec} (F)
0	36.27	354	1.5×10^{-8}
0.23	11.75	1025	1.1×10^{-8}