Supporting Information

Cesium Halides Assisted Crystal Growth of Perovskite Films for Efficient Planar Heterojunction Solar Cells

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Experimental Method

Materials: The commercial materials used are listed as followed: *N*, *N*-dimethylformamide (99.8%, Alfa Aesar), PbI_2 (99.999%, Alfa Aesar), CsI (99.999%, aladdin), CsBr (99.9%, Adamas), HI aqueous solution (55-57% w/w, Adamas), TiAcAc (75 wt % in isopropanol, Sigma-Aldrich), Absolute Ethanol (99.5%, aladdin), 2,2',7,7'-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spiro-bifluorene (Spiro-OMeTAD) (Woerjiming (Beijing) technical development institute), 4-tert-butylpyridine (96.0%, TCI), lithium bis(trifluoromethylsulfonyl)-imide (99.9%, Sigma-Aldrich), acetonitrile(99.9%, aladdin), chlorobenzene (99.9%, Sigma-Aldrich). $HC(NH_2)_2I$ (FAI), CH_3NH_3Cl (MACl) and TiO_2 nanocrystals were synthesized according to the literature report.[1-3]

Mobility measurements: The hole and electron mobility of perovskite films without and with Cs addition were measured by space-charge-limited-current (SCLC) method using a diode configuration of ITO/PEDOT:PSS/Perovskite/Spiro-OMeTAD/MoO_3/Ag for hole and ITO/TiO_2/ Perovskite /PCBM/BCP/Ag for electron by taking the dark current density in the range of 0–4 V and fitting the results to a space charge limited form, where the SCLC is described by:

$$J = \frac{9\varepsilon_0 \varepsilon_r \mu_0 V^2}{8L^3}$$

where J is the current density, L is the film thickness of the perovskite layer, μ_0 is the hole or electron mobility, ε_r is the relative dielectric constant of the transport medium, ε_0 is the permittivity of free space (8.85×10^{-12} F m^{-1}), V is the internal voltage in the device.[4]

Supporting Figures.

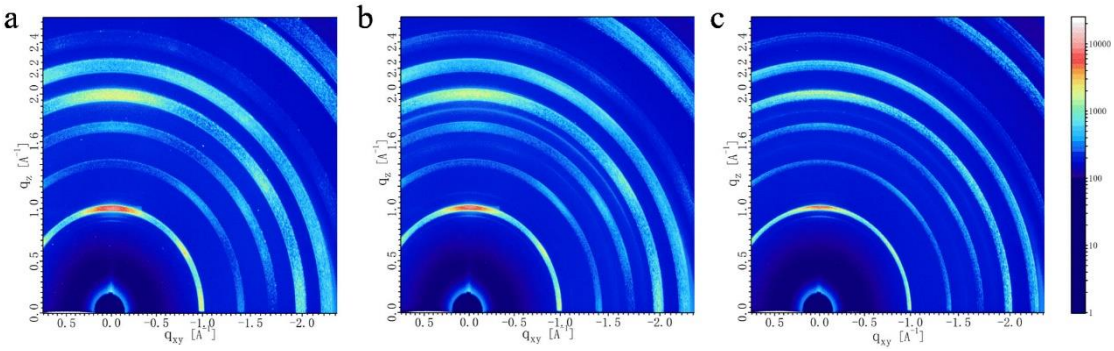

Figure S1. GIWAX patterns of (a) $FAPbI_3$(Cl), (b) $Cs_xFA_{1-x}PbI_3$(Cl) and (c) $Cs_xFA_{1-x}PbI_{3-x}Br_x$(Cl) perovskite films.

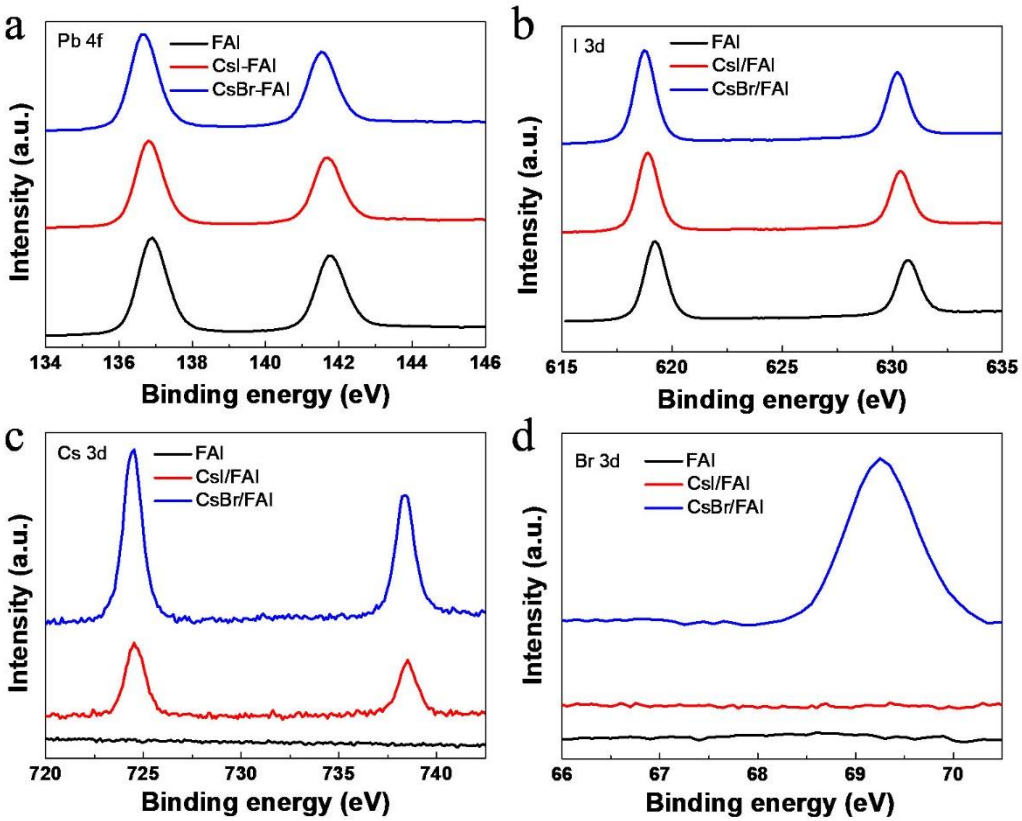

Figure S2. XPS spectra of $FAPbI_3$(Cl), $Cs_xFA_{1-x}PbI_3$(Cl) and $Cs_xFA_{1-x}PbI_{3-x}Br_x$(Cl) perovskite films.

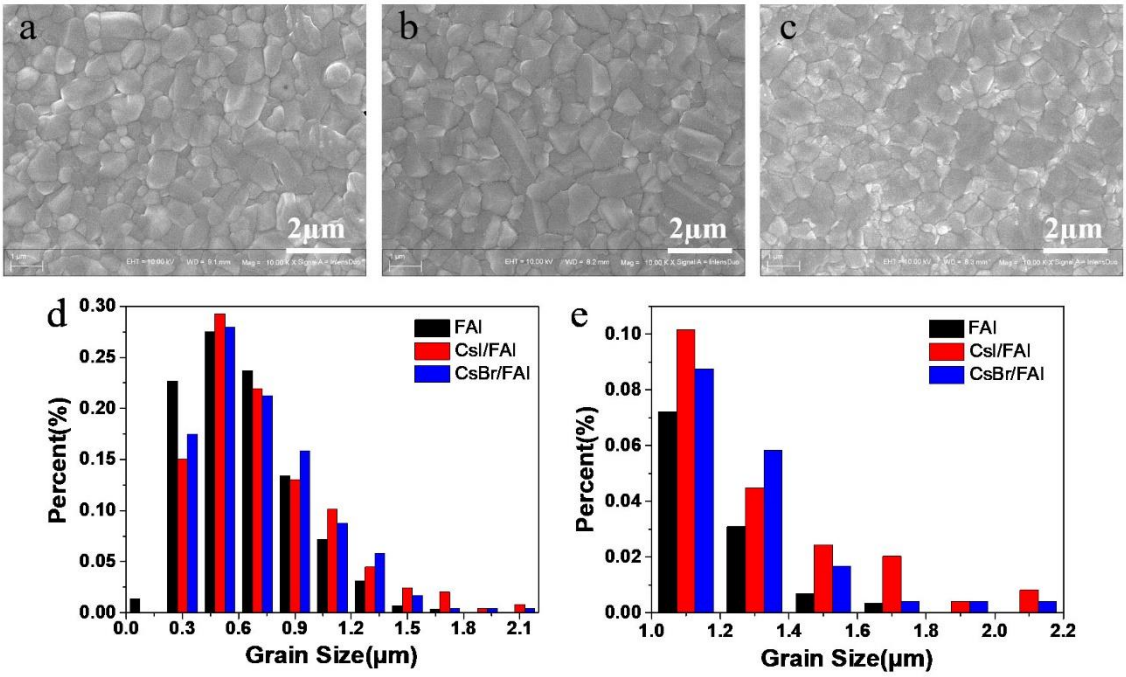

Figure S3. SEM images of (a) $FAPbI_3$(Cl), (b) $Cs_xFA_{1-x}PbI_3$(Cl) and (c) $Cs_xFA_{1-x}PbI_{3-x}Br_x$(Cl) films. (d, e) Grain size distribution extracted from SEM images of the $FAPbI_3$(Cl), $Cs_xFA_{1-x}PbI_3$(Cl) and $Cs_xFA_{1-x}PbI_{3-x}Br_x$(Cl) perovskite films.

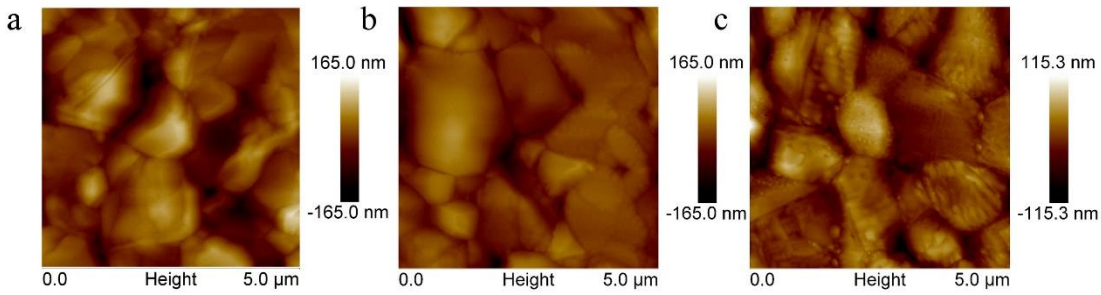

Figure S4. Taping-mode AFM height images (5 ×5 μm) of (a) $FAPbI_3$(Cl), (b) $Cs_xFA_{1-x}PbI_3$(Cl) and (c) $Cs_xFA_{1-x}PbI_{3-x}Br_x$(Cl) perovskite films.

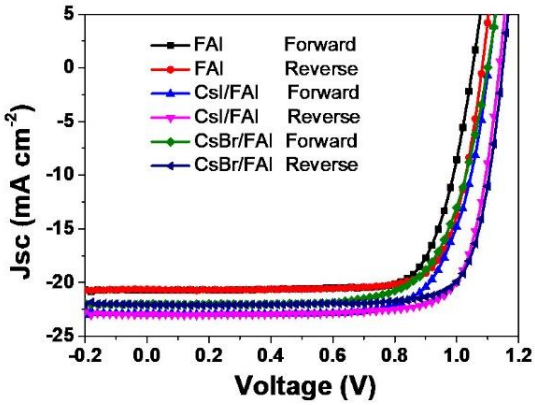

Figure S5. J-V curves of $FAPbI_3$(Cl), $Cs_xFA_{1-x}PbI_3$(Cl) and $Cs_xFA_{1-x}PbI_{3-x}Br_x$(Cl) based perovskite solar cells under different scan directions.

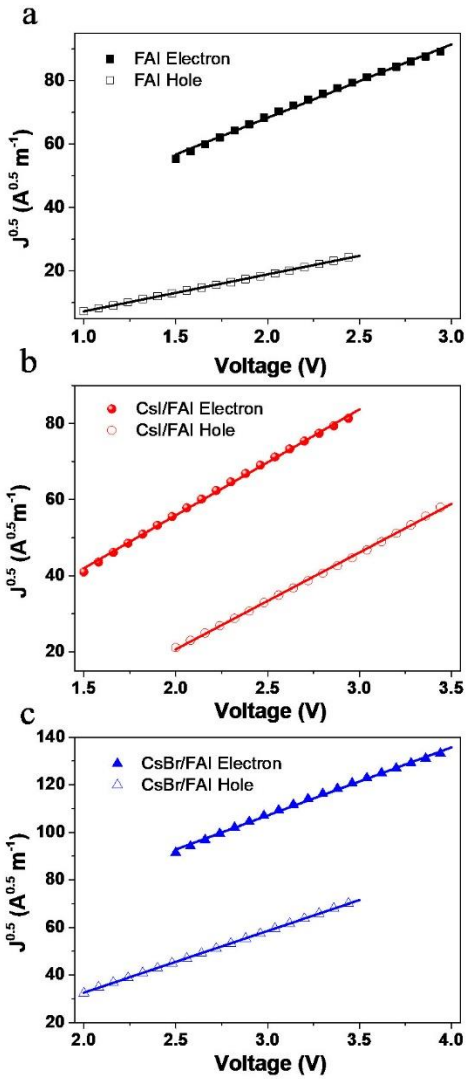

Figure S6. $J^{0.5}$-V plots for the (a) $FAPbI_3$(Cl), (b) $Cs_xFA_{1-x}PbI_3$(Cl) and (c) $Cs_xFA_{1-x}PbI_{3-x}Br_x$(Cl) based devices in the SCLC region.

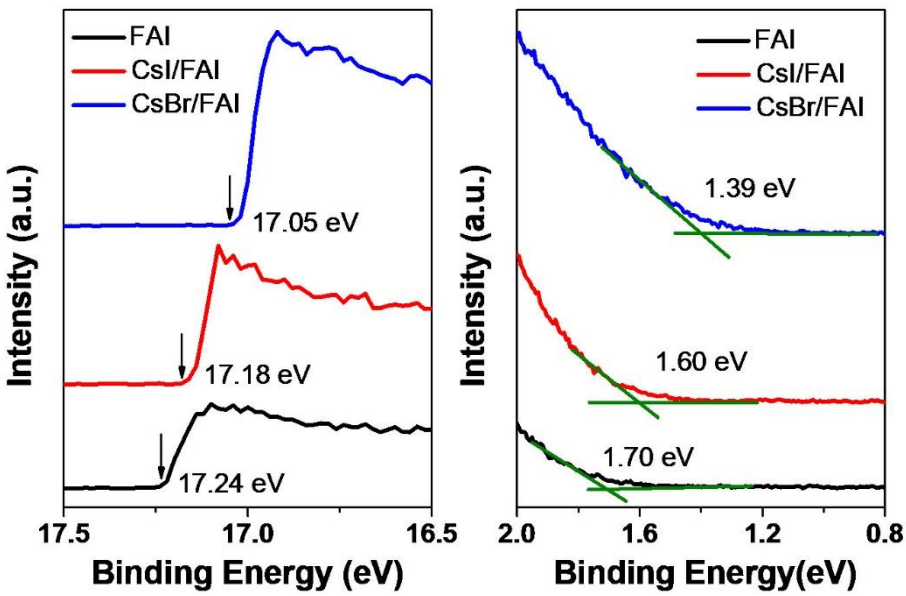

Figure S7. UPS spectra in the onset (right) and the cutoff (left) energy regions of the $FAPbI_3$(Cl), $Cs_xFA_{1-x}PbI_3$(Cl) and $Cs_xFA_{1-x}PbI_{3-x}Br_x$(Cl) perovskite films

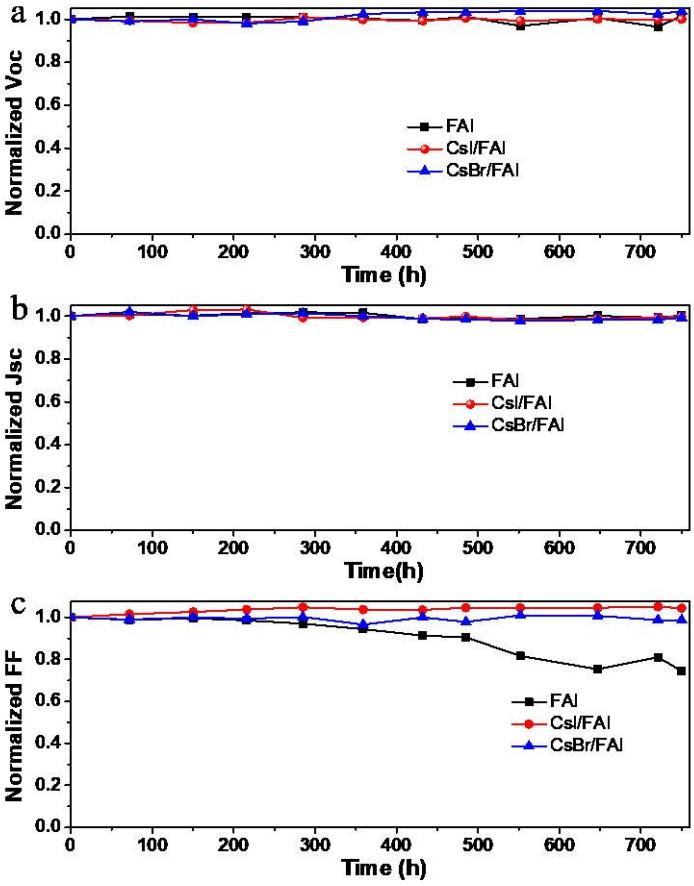

Figure S8. The stability of the corresponding perovskite solar cells stored in N_2 glove box without encapsulation.

Supporting tables.

Table S1. The full width at half maxima (FWHM) of $FAPbI_3$(Cl), $Cs_xFA_{1-x}PbI_3$(Cl) and $Cs_xFA_{1-x}PbI_{3-x}Br_x$(Cl) perovskite films.

Material	FWHM 2θ(°)
FAI	0.183
CsI/FAI	0.104
CsBr/FAI	0.096

Table S2. The statistical data of grain size distribution calculated from SEM images for $FAPbI_3$(Cl), $Cs_xFA_{1-x}PbI_3$(Cl) and $Cs_xFA_{1-x}PbI_{3-x}Br_x$(Cl) perovskite films.

Material	Grain Size	
	Average (nm)	>1 μm portion (%)
FAI	619	11.34
CsI/FAI	763	20.74
CsBr/FAI	730	17.50

Table S3. Representative perovskite devices performance under different scan directions.

Material	Direction	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	Efficiency (%)
FAI	Forward	1.05	20.73	75.83	16.52
	Reverse	1.08	20.62	77.12	17.21
CsI/FAI	Forward	1.10	22.83	73.13	18.42
	Reverse	1.13	23.02	77.81	20.38
CsBr/FAI	Forward	1.09	22.04	70.55	17.10
	Reverse	1.14	22.07	79.02	20.03

Table S4. Charge carrier mobility of the $FAPbI_3$(Cl), $Cs_xFA_{1-x}PbI_3$(Cl) and $Cs_xFA_{1-x}PbI_{3-x}Br_x$(Cl) perovskite thin films.

Material	μ_e ($cm^2 V^{-1} s^{-1}$)	μ_h ($cm^2 V^{-1} s^{-1}$)	μ_e/μ_h
FAI	1.37×10^{-3}	3.48×10^{-4}	3.94
CsI/FAI	1.98×10^{-3}	1.66×10^{-3}	1.19
CsBr/FAI	2.09×10^{-3}	1.72×10^{-3}	1.21

Table S5. Summary of the valance band (VB), conduction band (CB), Eg^{opt} and λ_{onset} for $FAPbI_3$(Cl), $Cs_xFA_{1-x}PbI_3$(Cl) and $Cs_xFA_{1-x}PbI_{3-x}Br_x$(Cl) perovskite films.

Material	VB (eV)[a]	CB (eV)[b]	Eg^{opt} (eV)	λ_{onset}(nm)
FAI	-5.55	-4.01	1.52	805.4
CsI/FAI	-5.63	-4.07	1.56	794.8
CsBr/FAI	-5.67	-4.10	1.57	790.3

[a)] Measured using UPS. [b)] Calculated by $E_{LUMO} = E_g - E_{HOMO}$.

References

[1] Lee, J. W.; Seol, D. J.; Cho, A. N.; Park, N. G. High-efficiency perovskite solar cells based on the black polymorph of $HC(NH_2)_2PbI_3$. *Adv. Mater.* **2014**, *26*, 4991-4998.

[2] Lee, M. M.; Teuscher, J.; Miyasaka, T.; Murakami, T. N.; Snaith, H. J. Efficient hybrid solar cells based on meso-superstructured organometal halide perovskites. *Science* **2012**, *338*, 643-647.

[3] Wang, J.; Polleux, J.; Lim, J.; Dunn. B. Pseudocapacitive Contributions to Electrochemical Energy Storage in TiO2(Anatase) Nanoparticles. *J. Phys. Chem. C* **2007**, *111*, 14925-14931.

[4] Shi, D.; Adinolfi, V.; Comin, R.; Yuan, M.; Alarousu, E.; Buin, A.; Chen, Y.; Hoogland, S.; Rothenberger, A.; Katsiev, K.; Losovyj, Y.; Zhang, X.; Dowben, P. A.; Mohammed, O. F.; Sargent, E. H.; Bakr. O. M. Solar cells. Low trap-state density and long carrier diffusion in organolead trihalide perovskite single crystals. *Science* **2015**, *347*, 519-522.