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Enhanced stability of α-phase $FAPbI_3$ perovskite solar cells by insertion of 2D $(PEA)_2PbI_4$ nanosheets

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1. Experimental details and additional data.

General: All materials were purchased from Sigma-Aldrich, TCI and Acros and used as received, unless stated otherwise.

$(PEA)_2PbI_4$ NSs prepared: 0.8 mmol of PEAI and 0.4 mmol of PbI_2 were dissolved in a mixture of 10 mL of DMF and 12.5 μL of *n*-octylamine to form a perovskite precursor solution. Then, 15 μL of the perovskite precursor solution was quickly dropped into 10 mL of methylene dichloride under vigorous stirring. The solution was centrifuged at 3,500 rpm for 3 min to remove the aggregated precipitates. Finally, the $(PEA)_2PbI_4$ NSs were obtained after centrifugation at 15,000 rpm for 5 min.

The prepared $(PEA)_2PbI_4$ NSs were dispersed in chlorobenzene (CB) for further use. To probe the effects of various concentrations of $(PEA)_2PbI_4$ NSs, they were dispersed in CB and were fixed the concentration at 6 mg mL^{-1}, 12 mg mL^{-1} and 18mg mL^{-1}.

Device Fabrication: FTO glass (Nippon sheet glass) substrates were sequentially cleaned with the detergent solution, acetone, and ethanol in an ultraphonic bath. A compact TiO_2 layer was then coated on the clean FTO substrate by spray pyrolysis deposition at 450 ^oC with a precursor solution prepared by diluting 900 μL titanium diisopropoxide in 15 ml ethanol. Mesoporous TiO_2 films were prepared using a diluted TiO_2 paste (Greatcell Solar 30 NR-D) in ethanol solution with weight ratio of 1:10. Films were spin-coated at 5000 rpm for 20 s, and sintered on a hot plate at 500 ^oC for 30 min. After cooling down to room temperature, a thin SnO_2 layer was deposited on the surface of mesoporous TiO_2 layer by spin-coating 1 mM $SnCl_4$ aqueous solution at 3000 rpm for 20 s, and finally baked at 190 ^oC for 1 h. The 1.2 M $Cs_{0.1}FA_{0.9}PbI_3$ precursor solution was prepared by mixing CsI (31.2 mg), PbI_2 (553.38 mg) and FAI (185.78 mg) in mixed solvent of 800 μl DMF

and 200 μl DMSO. Then, $Cs_{0.1}FA_{0.9}PbI_3$ precursor solution was spin-coated at 1000 rpm for 10 s and continuously at 4000 rpm for 30 s. During the second step, 100 μl of CB with/without $(PEA)_2PbI_4$ NSs was poured 15 seconds before the process was finished. The substrates were annealed at 150 ^oC for 10 min. Finally, Spiro-OMeTAD was spin-coated at 4000 rpm for 20 s. The Spiro-OMeTAD solution was prepared by dissolving in chlorobenzene at 70 mM and adding 4-tert-butylpyridine, Li-TFSI in acetonitrile, and $Co[t\text{-}BuPyPz]_3[TFSI]_3$ (FK209) in acetonitrile at the molar ratio of Spiro-OMeTAD: FK209 : LiTFSI : TBP of 1 :0.03: 0.5: 3.3. Devices were fabricated with a 70 nm thick gold counter electrode by using thermal evaporation.

For SCLC measurement. Electron-only device is fabricated as follows: FTO/c-TiO_2/m-TiO_2/perovskite layers are deposited in the same way of PSCs. After cooling down perovskite layer, PCBM solution (20 $mg \cdot ml^{-1}$ in CB) was spin-coated on perovskite at 1500 rpm for 30 s, and then heated at 70 ^oC for 10 min. And finally, 70 nm thick gold counter electrode by using thermal evaporation. hole-only device is fabricated as follows: PEDOT:PSS was spin-coated on clean FTO at 2500 rpm for 40 s, and then heated at 120 ^oC for 10 min. Perovskite and spiro-OMeTAD layers were deposited the same as PSCs. At last, 70 nm thick gold counter electrode by thermal evaporation.

Film and device characterization. X-ray diffraction (XRD) analysis was carried out using a Bruker D8 Advance diffractometer in an angle range of $2\theta = 5°$ to 45°. The glancing-angle incidence XRD measurements were carried out with glancing angle ranging from 0.3° to 4°. The morphology of the films was characterized using a high resolution scanning electron microscope (SEM, ZEISS Merlin). It was carried out two days after preparing the films. The absorbance and reflectance were measured with an integrating sphere using UV/Vis/NIR spectroscopy (PerkinElmer Lambda). The steady-state PL and time-resolved PL spectra were record by a lab-built spectrophotometer under

395 nm excitation. The PL life time was obtained by fitting the time-resolved PL spectra via biexphnential decay functions. The solar cell measurement was done using commercial solar simulators (Oriel, 450 W Xenon, AAA class/Oriel VeraSol-2, LED, AAA class). The light intensity was calibrated with a Si reference cell equipped with an IR-cutoff filter (KG5, Newport), and it was recorded before each measurement. Current–voltage characteristics of the cells were obtained by applying an external voltage bias while measuring the current response using a digital source meter (Keithley 2400/2604). The voltage scan rate was 10 or 25 mV s^{-1} and no device preconditioning such as light soaking, or forward voltage bias applied for a long time, was applied before starting the measurement. The cells were masked with an active area of 0.16 cm^2 to fix the active area and reduce the influence of the scattered light. EQE was measured by IQE200B (Oriel) under the monochromatic light intensity calibrated by a reference silicon detector.

2. Additional Data

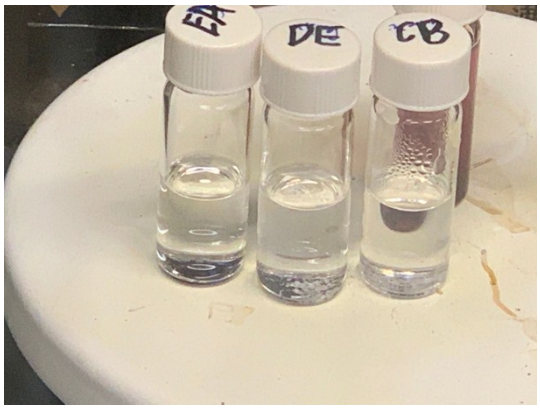

Figure S1. 1 mg PEAI was dissolved in ethyl acetate (EA), diethyl ether (DE), and chlorobenzene (CB) respectively under heated at 60 ℃ for 6 hours.

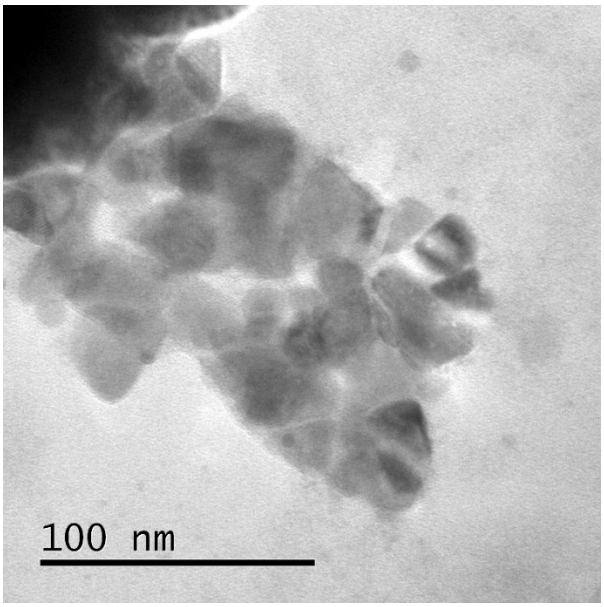

Figure S2. TEM image of 2D $(PEA)_2PbI_4$ nanosheets

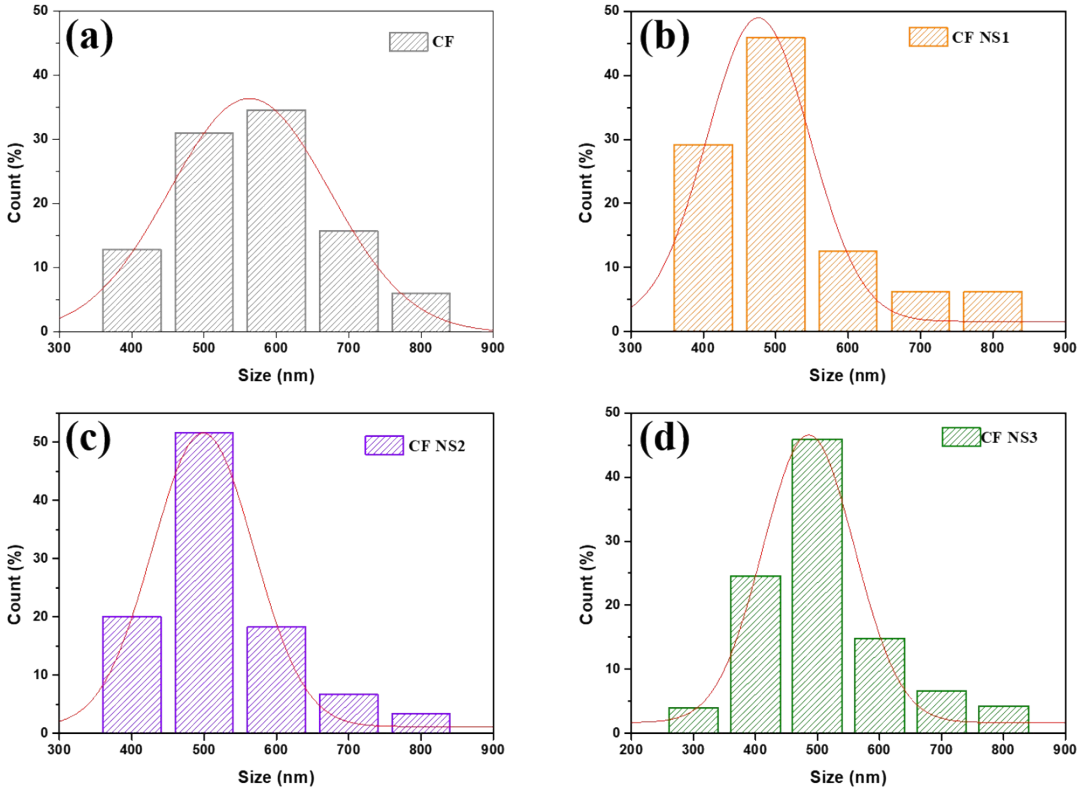

Figure S3. The grain size statistics of $Cs_{0.1}FA_{0.9}PbI_3$ perovsktie thin films: (a) CF, (b) CF NS1, (c) CF NS2 and (d) CF NS3.

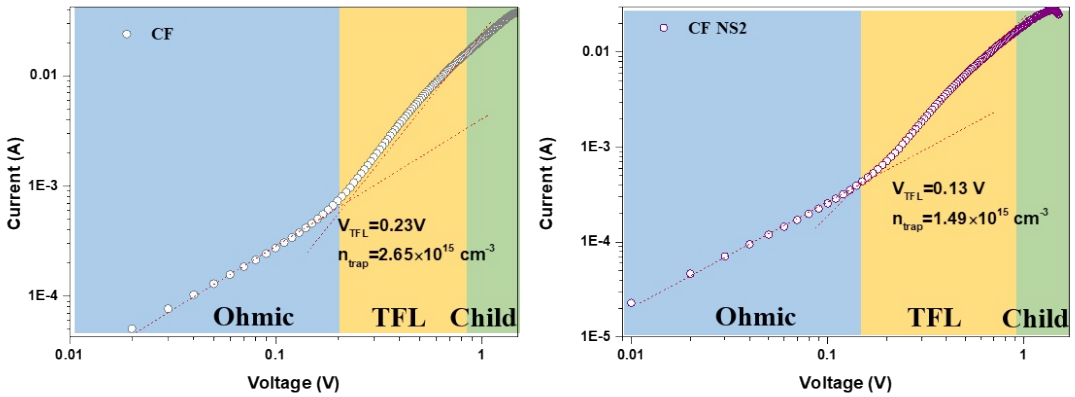

Figure S4. The space charge-limited current versus voltage of electron-only device based-on (a) CF and (b) CF NS2.

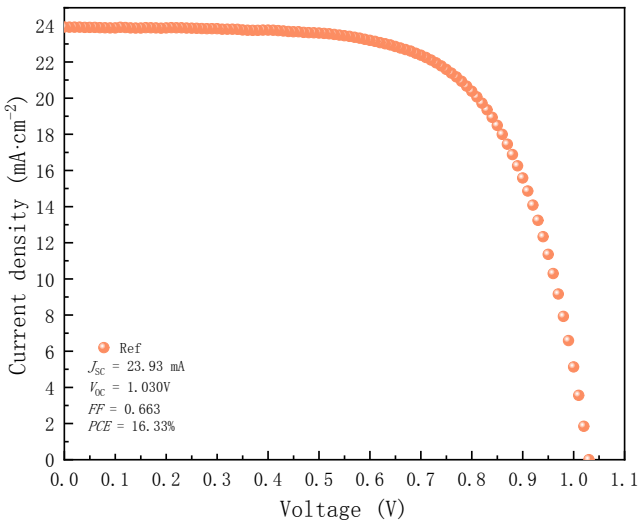

Figure S5. J-V curves of the device based-on CF with 1% PEAI doping under reverse scan direction.

Table S1. Fitting parameters for the time-resolved PL spectra of CF and CF NS2 perovskite thin films. The fitting equation is $y = A_1*\exp(-x/\tau_1) + A_2*\exp(-x/\tau_2)$.

Sample	R^2	τ_{avg} (ns)
CF	0.996	66.14
CF NS2	0.982	186.08

Table S2. Fitting parameters for the time-resolved PL spectra of CF and CF NS2 perovskite thin films with ETL (TiO_2) and HTL (spiro-OMeTAD). The fitting equation is $y = A_1*\exp(-x/\tau_1) + A_2*\exp(-x/\tau_2)$.

Sample	R^2	τ_{avg} (ns)
CF/TiO_2	0.975	161.70
CF NS2/TiO_2	0.998	20.69
CF/spiro-OMeTAD	0.998	30.96
CFNS2/spiro-OMeTAD	0.997	20.38

Table S3. The photovoltaic performance summary of devices based on CF NS2

Sample	Scan direction	J_{sc} (mA/cm^2)	Ave J_{sc} (mA/cm^2)	V_{oc} (V)	Ave V_{oc} (V)	*FF*	Ave *FF*	*PCE* (%)	Ave *PCE* (%)
NS2	RS	24.67	24.68	1.054	1.045	0.779	0.776	20.27	20.01
	FR	24.68		1.036		0.773		19.75	

Table S4. The photovoltaic performance summary of devices based on CF and CF NS2, which were collected from the J-V curve under reverse scan direction.

CF	J_{sc} (mA/cm^2)	V_{oc} (V)	*FF*	*PCE* (%)	CF NS 2	J_{sc} (mA/cm^2)	V_{oc} (V)	*FF*	*PCE* (%)
	24.64	0.9659	0.75	17.86		24.83	1.059	0.778	20.44
	24.64	0.9515	0.746	17.49		24.44	1.063	0.753	19.58
	24.99	0.9632	0.75	18.07		24.85	1.037	0.754	19.44
	25.08	0.964	0.738	17.84		24.46	1.055	0.758	19.57
	24.51	0.9731	0.754	17.99		24.88	1.063	0.743	19.65
	24.66	0.9626	0.732	17.38		24.7	1.089	0.761	20.45
	24.46	0.9683	0.744	17.61		24.64	1.07	0.74	19.52
	24.78	0.9607	0.731	17.4		24.37	1.085	0.761	20.12
	24.81	0.9608	0.738	17.58		24.76	1.076	0.762	20.3
	24.52	0.9658	0.741	17.54		24.69	1.085	0.751	20.1
	24.65	0.9686	0.746	17.82		24.96	1.058	0.738	19.49
	24.73	0.9628	0.746	17.77		24.85	1.041	0.75	19.4
	24.74	0.9814	0.759	18.44		24.85	1.037	0.754	19.44
	24.99	0.9632	0.742	17.85		24.88	1.063	0.743	19.65
	24.95	0.9949	0.722	17.91		25.04	1.044	0.74	19.34
	24.94	1.015	0.713	18.03		24.9	1.044	0.745	19.37
	24.62	1.007	0.729	18.08		24.51	1.04	0.757	19.3
	24.66	1.014	0.724	18.11		24.65	1.049	0.745	19.26
	24.86	0.9773	0.747	18.15		25.05	1.075	0.744	20.03
	25.05	0.9746	0.744	18.17		25.04	1.067	0.758	20.25
	24.85	1.008	0.728	18.23		25.07	1.068	0.757	20.27

	25.14	0.9609	0.755	18.24		24.93	1.076	0.758	20.33
	24.99	1.004	0.727	18.24		25.09	1.064	0.747	19.94
	24.99	1.023	0.716	18.31		24.44	1.043	0.76	19.36
	24.66	1.032	0.72	18.33		24.85	1.045	0.773	20.06
Avg.	24.79	0.957	0.752	17.83		24.96	1.023	0.762	19.46