Electronic Supplementary Material (ESI) for Energy Advances.

Supporting Information

Stress-induced stabilization of photoactive $FAPbI_3$ phase in ambient conditions without using an additive approach

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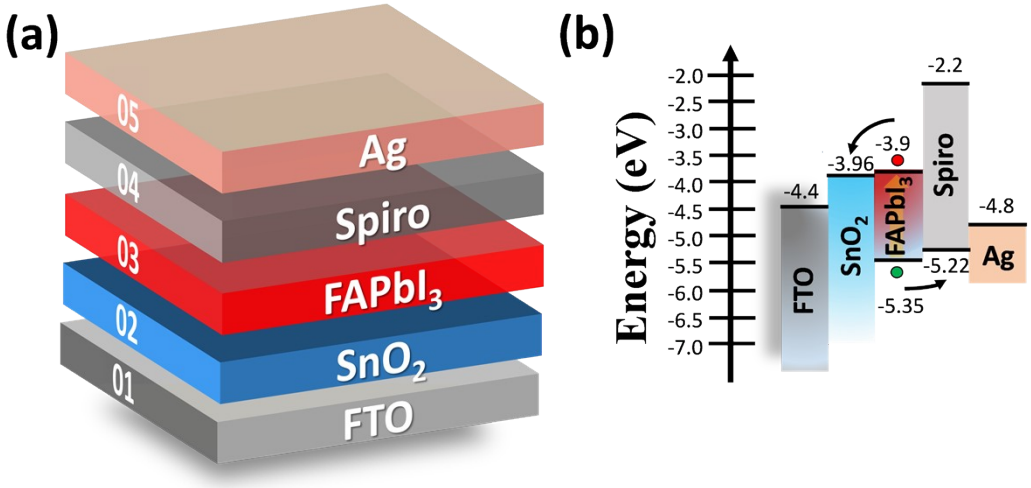

Figure S1: Schematic of Perovskite solar cells (a) Device architecture, and (b) Energy-Band diagram of the device. The energy band positions have been taken from various references.[1-5]

Table S1: Systematic exploration of solvent ratio and anti-solvent selection in conjunction with Two and Three-Step spin coating parameters for the deposition of Perovskite Films on both SnO_2-coated FTO substrates and Glass substrates.

Note: The perovskite Films formed under RH = 20-28%, Temperature = 24-30 °C.

Solvent	**FAI: PbI_2 Molar Ratio**	**Anti-solvent**	**Annealing Temperature (°C)**	**Formation of α-$FAPbI_3$ With spin coating parameters**
DMF: DMSO (9:1)	1.5 M 1 M 0.7 M	Chlorobenzene Toluene Ethyl Acetate	150-170	2-step; N 3-step; N
DMF: DMSO (4:1)	1.5 M 1 M 0.7 M	Chlorobenzene Toluene Ethyl Acetate	150-170	2-step; N 3-step; N

DMF: DMSO (3:1)	1.5 M 1 M 0.7 M	Chlorobenzene Toluene Ethyl Acetate	150-170	2-step; N 3-step; Y only with 0.7M ratio of FAI: PbI_2 but not with Ethyl Acetate

N: Perovskite film not formed; Y: Perovskite film formed.

Table S2: Optimization of spin coating parameters, anti-solvent dripping duration, anti-solvent volume, and annealing temperature for the precision fabrication of Perovskite Films on Glass substrates and SnO_2-coated FTO substrates.

Spin coating Steps	**Spin coating parameters**	**Anti-solvent Dripping During the deposition process**	**Anti-solvent**	**Temperature (℃)**	**Formation of α-$FAPbI_3$**
2-step	1200 rpm, 15 sec 5000 rpm, 30 sec	15th sec of second step	Chlorobenzene (250-300μL)	150-170	Not formed
2-step	1200 rpm, 15 sec 5000 rpm, 30 sec	15th sec of second step	Toluene (250-300μL)	150-170	Not formed
3-step	500 rpm, 5sec 3500 rpm, 5 sec 5000 rpm, 30 sec	Ending of second step	Chlorobenzene (250-300μL)	150-170	Very poor-quality film formed
3-step	500 rpm, 5sec 3500 rpm, 5 sec 5000 rpm, 30 sec	Ending of second step	Toluene (250-300μL)	150-170	Poor quality film formed
3-step	500 rpm, 5sec 3500 rpm, 5 sec 5000 rpm, 30 sec	During acceleration of 3rd step	Toluene (250-300μL)	150-170	Poor quality film formed but slide improvement from previous one
3-step	500 rpm, 5sec 3500 rpm, 5 sec 5000 rpm, 30 sec	Starting of third step	Toluene (250-300μL)	150-170	Poor quality film formed but slide improvement from previous one
3-step	500 rpm, 5sec 3500 rpm, 5 sec 5000 rpm, 30 sec	7th sec of third step	Toluene (250-300μL)	150-170	Poor quality film formed but slide improvement from previous one
3-step	500 rpm, 5sec	12th sec of third step	Toluene	150-170	Poor quality film formed but slide improvement

	3500 rpm, 5 sec 5000 rpm, 30 sec		(250-300μL)		from previous one
3-step	500 rpm, 5sec 3500 rpm, 5 sec 5000 rpm, 30 sec	15th sec of third step	Toluene (250-300μL)	150-170	Good quality film formed
3-step	500 rpm, 5sec 3500 rpm, 5 sec 5000 rpm, 30 sec	15th sec of third step	Toluene (250μL)	150-170	Good quality film formed slide improvement from previous one
3-step	**500 rpm, 5sec 3500 rpm, 5 sec 5000 rpm, 30 sec**	**15th sec of the third step**	**Toluene (250μL)**	**150**	**Very Good quality film formed**
3-step	500 rpm, 5sec 3500 rpm, 5 sec 5000 rpm, 30 sec	18th sec of the third step	Toluene (250μL)	150	Very poor-quality film formed

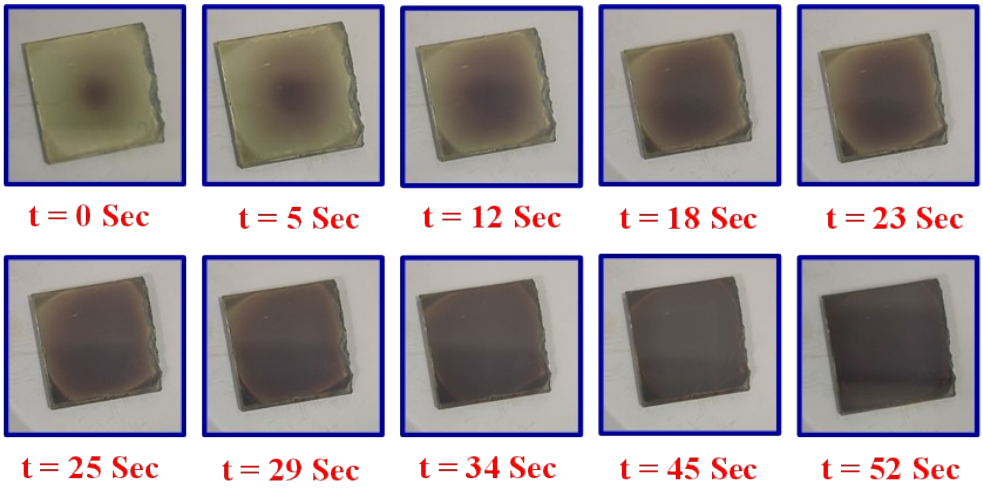

Figure S2: Phase transformation images from intermediate to $FAPbI_3$ phase with different time intervals after reaching 150 ℃.

Table S3: Theoretical stress calculation at various temperatures, while perovskite solution temperature was constant at 70℃.

$E_P / 1 - \upsilon_P$	$\alpha_s - \alpha_P$	$\alpha_g - \alpha_P$	**Substrate Temperature (℃)**	ΔT	**Stress in Sample S1 (MPa)**	**Stress in Sample S2 (MPa)**
15.857 GPa	10^{-5} K^{-1}	10^{-4} K^{-1}	30	+40	+63.43	+6.34
			40	+30	+47.57	+4.75
			50	+20	+31.71	+3.17
			60	+10	+15.85	+1.58
			70	0	0	0
			80	-10	-15.85 (Compressive stress)	-1.58 (Compressive stress)

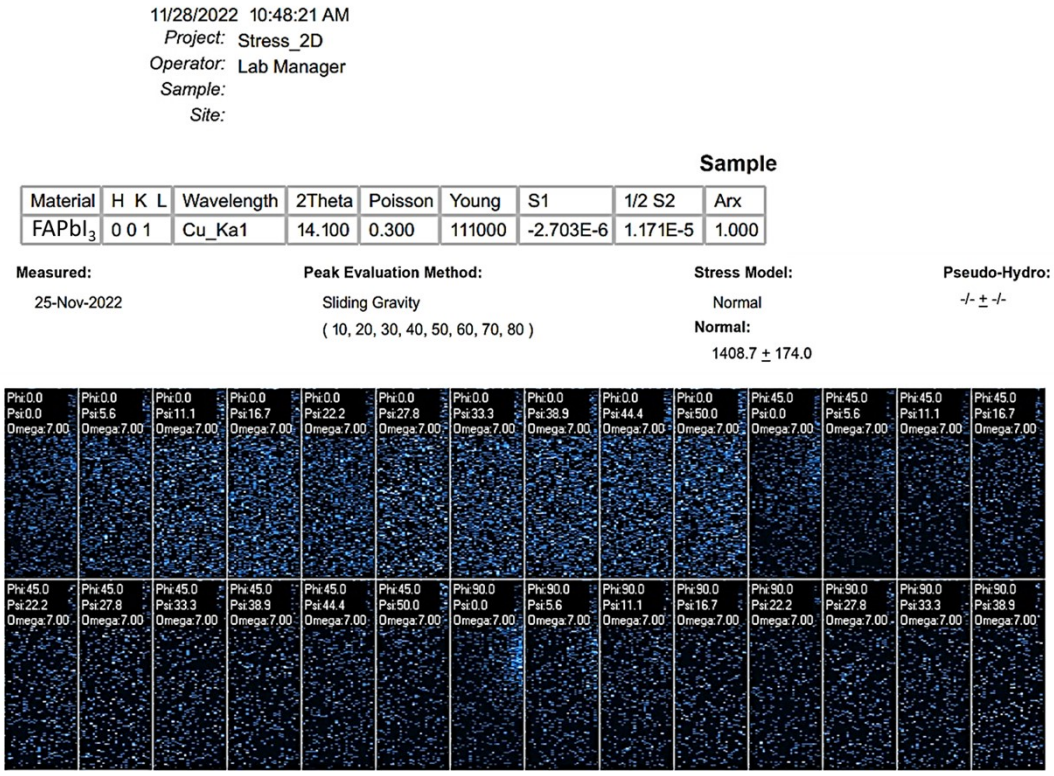

Figure S3: Stress analysis of Glass/FTO/SnO_2/$FAPbI_3$ based film using XRD

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Project: Stress_2D
Operator: Lab Manager
Sample:
Site:

Sample

Material	H K L	Wavelength	2Theta	Poisson	Young	S1	1/2 S2	Arx
$FAPbI_3$	0 0 1	Cu_Ka1	14.100	0.300	111000	-2.703E-6	1.171E-5	1.000

Measured: 25-Nov-2022

Peak Evaluation Method: Gravity (30)

Stress Model: Normal

Normal: 29.6 ± 50.2

Pseudo-Hydro: -/- ± -/-

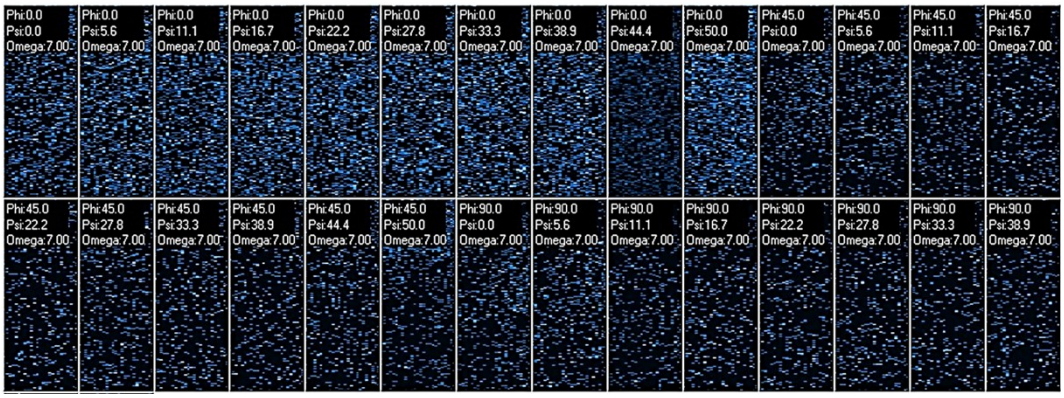

Figure S4: Stress analysis of Glass/$FAPbI_3$ based film using XRD.

Table S4: Mechanical properties and XRD peak at (001) of $FAPbI_3$ film.[6-8]

Plane	**(001)**
2θ	14.1
Poisson's ratio	0.3
Young Modulus	11.1 GPa

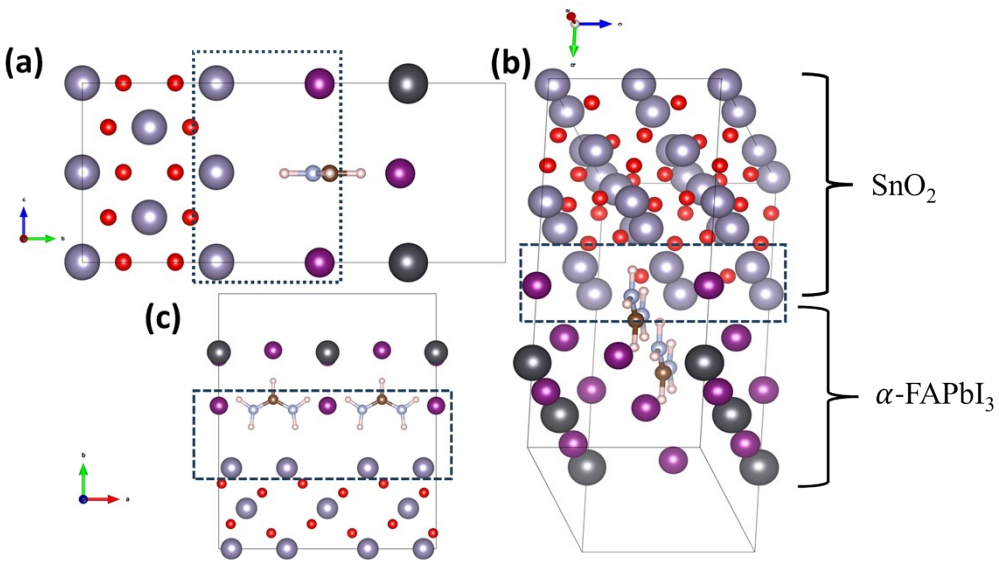

Figure S5: Shows the atomic structure model of the $FAPbI_3/SnO_2$ interfacial mismatch (dotted lines) at the different axis, (a) 2D structure in the b-c direction, (b) 3D structure, and (c) 2D structure in the a-b direction.

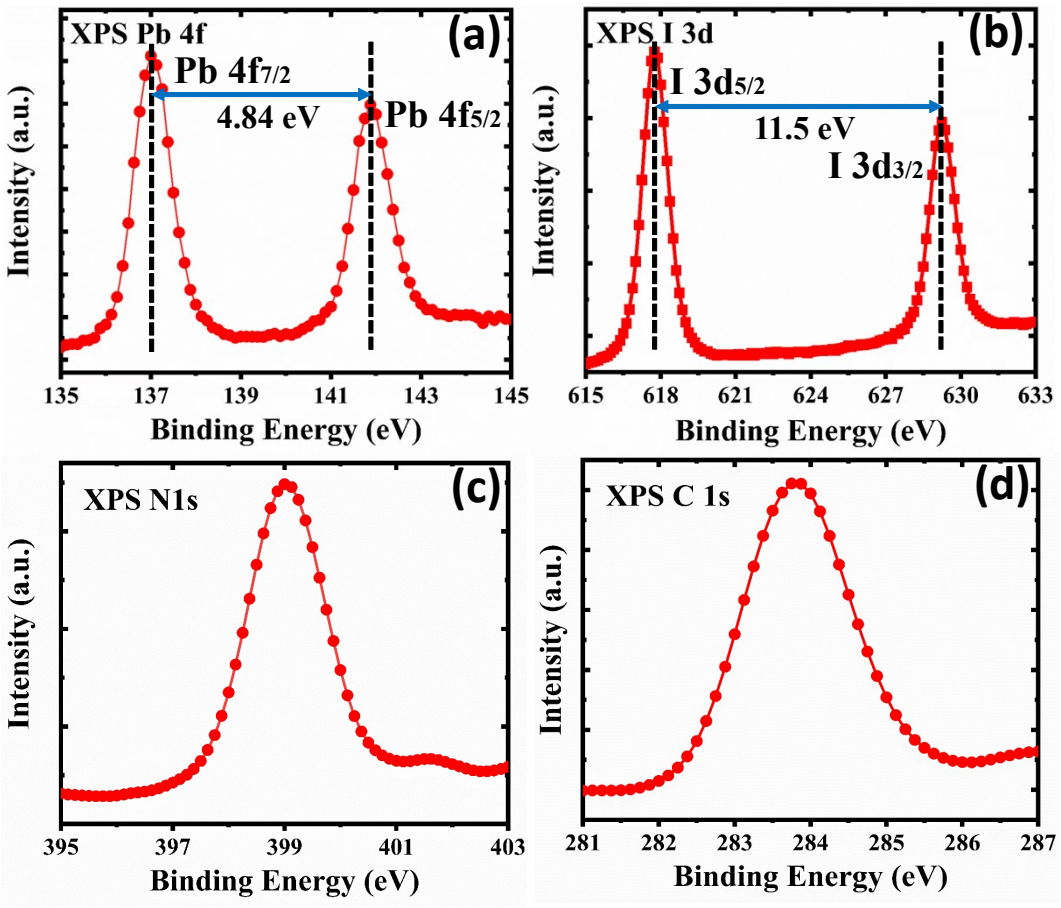

Figure S6: XPS spectra of $FAPbI_3$ film; (a) Pb 4f, (b) I 3d, (c) N1s, and (d) C1s.

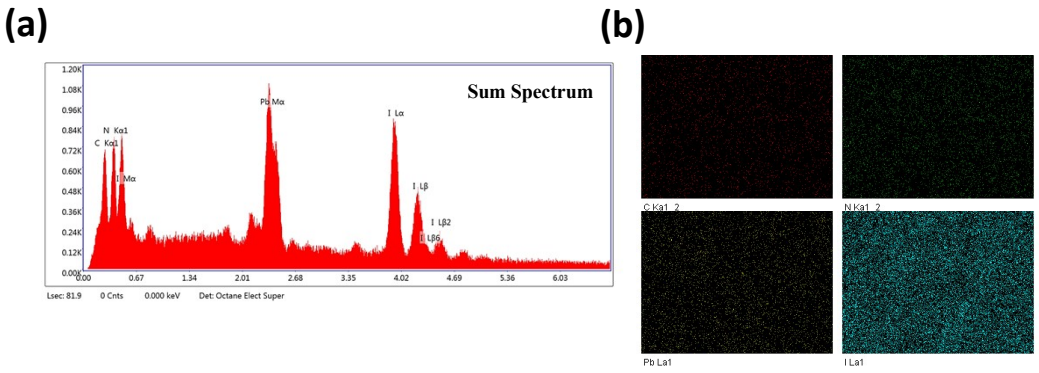

Figure S7: EDS Spectral analysis; (a) EDS sum spectrum of $FAPbI_3$, and (b) Elemental mapping of C, N, Pb and I in the perovskite structure

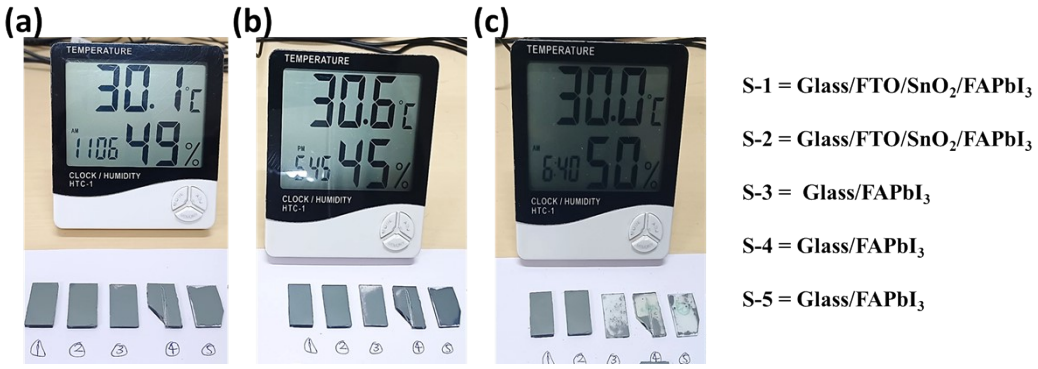

Figure S8: Stability of α-$FAPbI_3$ film at different substrates; (a) At 0-hour (fresh film), (b) film after 6 hours, and (c) film after 20 hours.

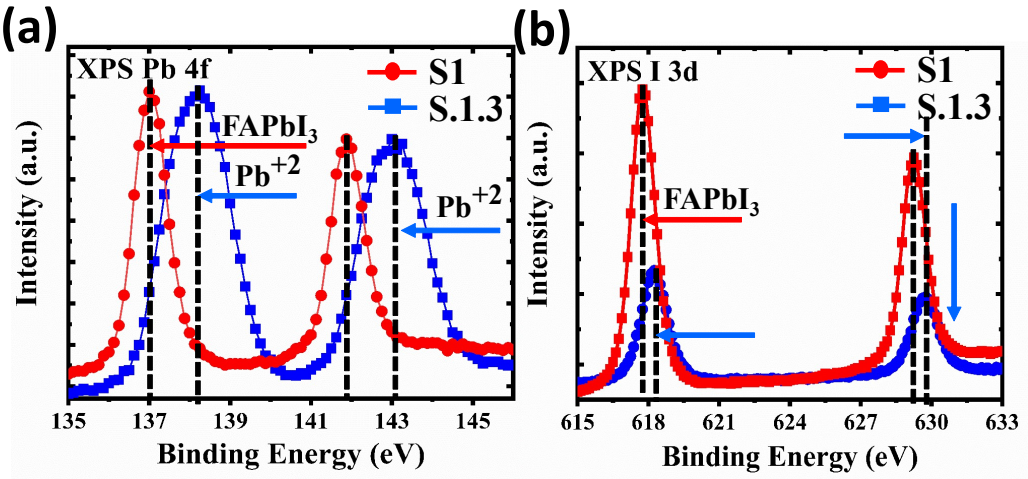

Figure S9: XPS spectra of Pb 4f, I 3d (S1) fresh film, and (S1.3) three months aged sample.

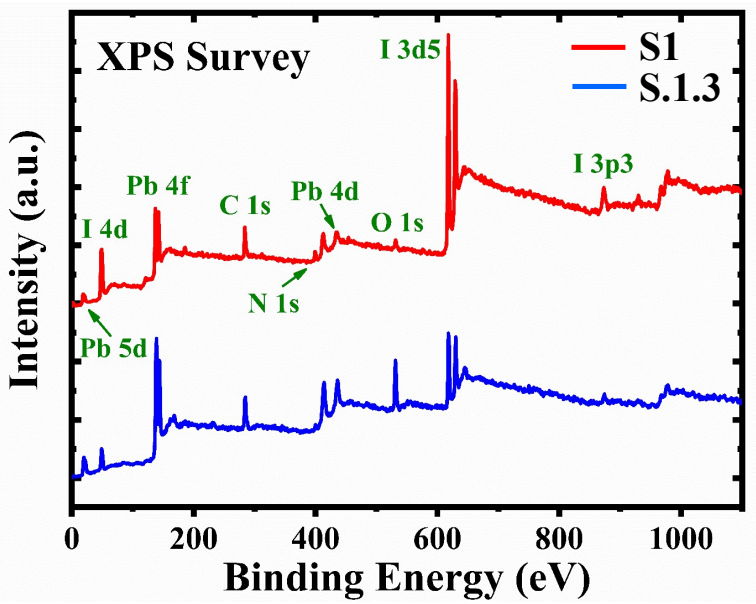

Figure S10: XPS survey of; (S1) fresh film, and (S1.3) three months aged sample.

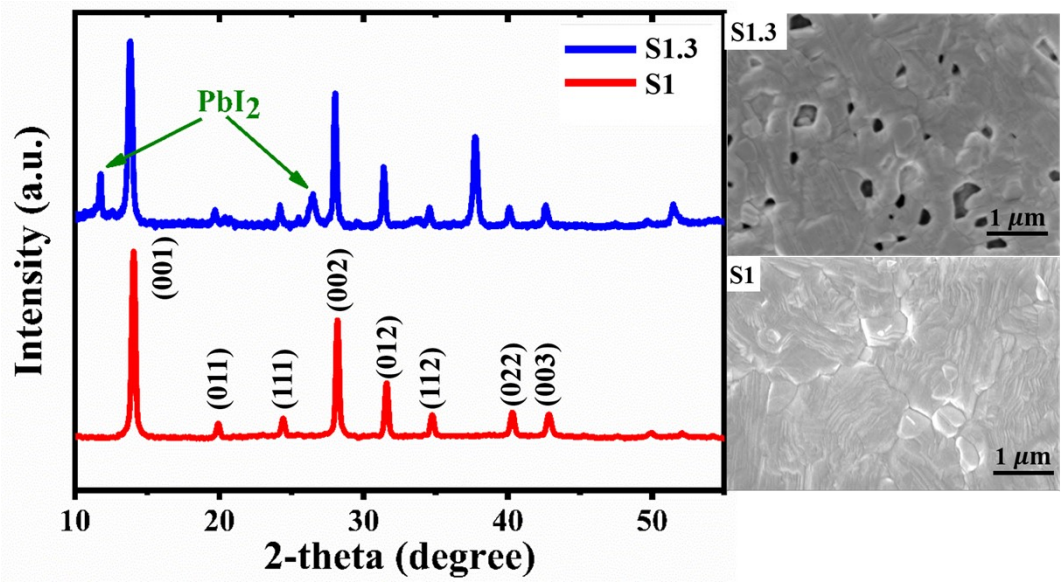

Figure S11: XRD pattern and SEM images (top-view) of α-$FAPbI_3$ film on Glass/FTO/SnO_2 coated substrates; (S1) fresh film, and (S1.3) three months aged sample.

Table S5: Average experimental data for the photovoltaic performance of 25 devices in reverse direction.

Device data of 25 cells	J_{SC} (mA/cm^2)	V_{OC} (V)	FF (%)	Efficiency (%)
	25.7 ± 0.5	1.031 ± 0.024	68.2 ± 5.4	18.26 ± 2.2

References:

1. Y. Chen, Y. Lei, Y. Li, Y. Yu, J. Cai, M.-H. Chiu, R. Rao, Y. Gu, C. Wang, W. Choi, H. Hu, C. Wang, Y. Li, J. Song, J. Zhang, B. Qi, M. Lin, Z. Zhang, A. E. Islam, B. Maruyama, S. Dayeh, L.-J. Li, K. Yang, Y.-H. Lo and S. Xu, *Nature*, 2020, **577**, 209-215.
2. J. Zhao, Y. Zhang, X. Zhao, J. Zhang, H. Wang, Z. Zhu and Q. Liu, *ACS Applied Energy Materials*, 2019, **2**, 2034-2042.
3. J. H. Lee, D. Shin, R. Rhee, S. Yun, K. M. Yeom, D. H. Chun, S. Lee, D. Kim, Y. Yi, J. H. Noh and J. H. Park, *The Journal of Physical Chemistry Letters*, 2019, **10**, 6545-6550.
4. D. Liu, S. Ren, X. Ma, C. Liu, L. Wu, W. Li, J. Zhang and L. Feng, *RSC Advances*, 2017, **7**, 8295-8302.
5. J. Wang, J. Li, Y. Zhou, C. Yu, Y. Hua, Y. Yu, R. Li, X. Lin, R. Chen, H. Wu, H. Xia and H.-L. Wang, *Journal of the American Chemical Society*, 2021, **143**, 7759-7768.
6. M. Dailey, Y. Li and A. D. Printz, *ACS Omega*, 2021, **6**, 30214-30223.
7. S. Sun, F. H. Isikgor, Z. Deng, F. Wei, G. Kieslich, P. D. Bristowe, J. Ouyang and A. K. Cheetham, *ChemSusChem*, 2017, **10**, 3740-3745.
8. E. C. Schueller, G. Laurita, D. H. Fabini, C. C. Stoumpos, M. G. Kanatzidis and R. Seshadri, *Inorganic Chemistry*, 2018, **57**, 695-701.