Science Advances
AAAS

advances.sciencemag.org/cgi/content/full/5/10/eaaw6619/DC1

Supplementary Materials for

Nanoscale mapping of chemical composition in organic-inorganic hybrid perovskite films

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Published 25 October 2019, *Sci. Adv.* **5**, eaaw6619 (2019)
DOI: 10.1126/sciadv.aaw6619

This PDF file includes:

Supplementary Materials

Perovskite preparation

CsI (99.9 %), PbI_2 (99 %), $PbBr_2$ (99 %) were purchased from Sigma-Aldrich. All chemicals were used without further purification. Methylammonium bromide (CH_3NH_3Br, MABr) was synthetized by a reaction of an equimolar amount of hydrobromic acid (HBr, 48 %, Aldrich) with methylamine (CH_3NH_2, 40% in water, Aldrich). The mixture was stirred for 2 h at 0ºC, then the solvent was evaporated at 50ºC under reduced pressure. Formamidinium iodide ($CH(NH_2)_2I$, FAI) was synthetized by a reaction of hydriodic acid (HI, 57% in water, Aldrich) and formamidine acetate (FAAc, Aldrich) with 3x molar excess of HI. The FAAc was dissolved in methanol and HI was slowly added into the solution. The solution was left stirring for 30 minutes then the solvent was evaporated at 50ºC under reduced pressure. The products of MABr and FAI reactions were dissolved in ethanol, recrystallized using diethyl ether, filtrated and then dried in a vacuum oven at 50ºC for 12h. PbI_2 and $PbBr_2$ were dissolved in a mixed solvent of dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) (v/v =1/4) and stirred for 3h at 100ºC to completed dissolution of the inorganic salts. After cooling to room temperature, MABr, FAI and CsI were added to obtain the perovskites $Cs_{0.05}FA_{0.79}MA_{0.16}PbI_{2.49}Br_{0.51}$ (CsFAMA). To $FA_{0.83}MA_{0.17}PbI_{2.49}Br_{0.51}$ (FAMA), MABr and FAI were added. The concentration of the CsFAMA and FAMA solution were 0.8M and 1.2M, respectively. The solutions were left stirring for 30 minutes before perovskite deposition. The perovskites solutions were spin coated onto silicon substrates covered with 80 nm of gold inside of a glovebox filled with nitrogen. Spin coating contained a two-step procedure with the first step of 1000 ramp for 10 s and the last step of 4000 rpm for 30 s. 200 µL of chlorobenzene was applied on the spinning substrates at 10 s of the second step. After the spin coating, the substrates were annealed at 100ºC for 60 minutes.

Solar cell characterization

A device based solar cell was prepared and characterized in terms of current density as function of voltage, as seen in fig. S1. The conversion efficiency of this device attained 20.17% and 19.20% in backward and forward scans, respectively. Figure S2 shows the high-resolution cross-section SEM image of the device.

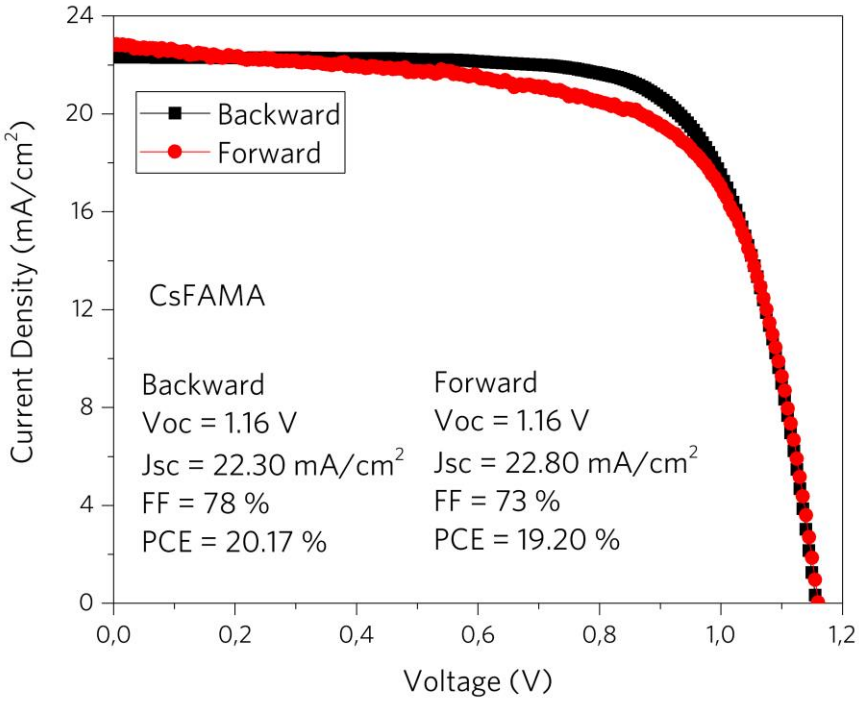

Fig. S1. Photovoltaic performance of CsFAMA solar cell. J-V curves of CsFAMA ($Cs_{0.05}FA_{0.79}MA_{0.16}Pb(I_{0.83}Br_{0.17})_3$ device with configuration FTO/TiO_2/CsFAMA/spiro-OMeTAD/Au measured under AM1.5G illumination.

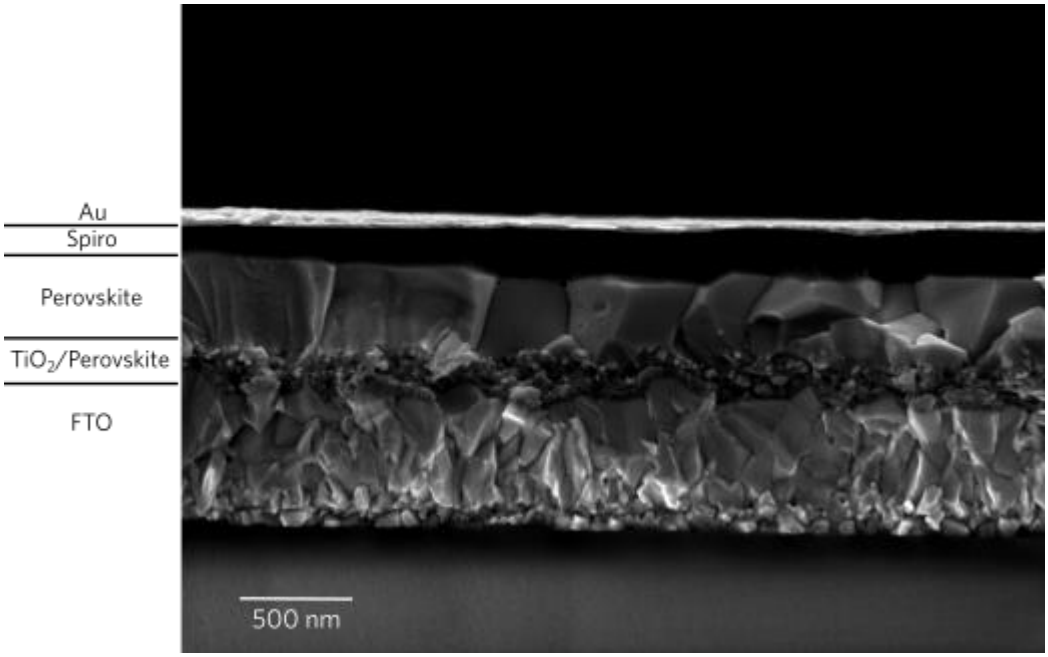

Fig. S2. High-resolution cross-sectional SEM image of the device. The SEM image reveals a film composed by a monolayer of perovskite grains in CsFAMA device.

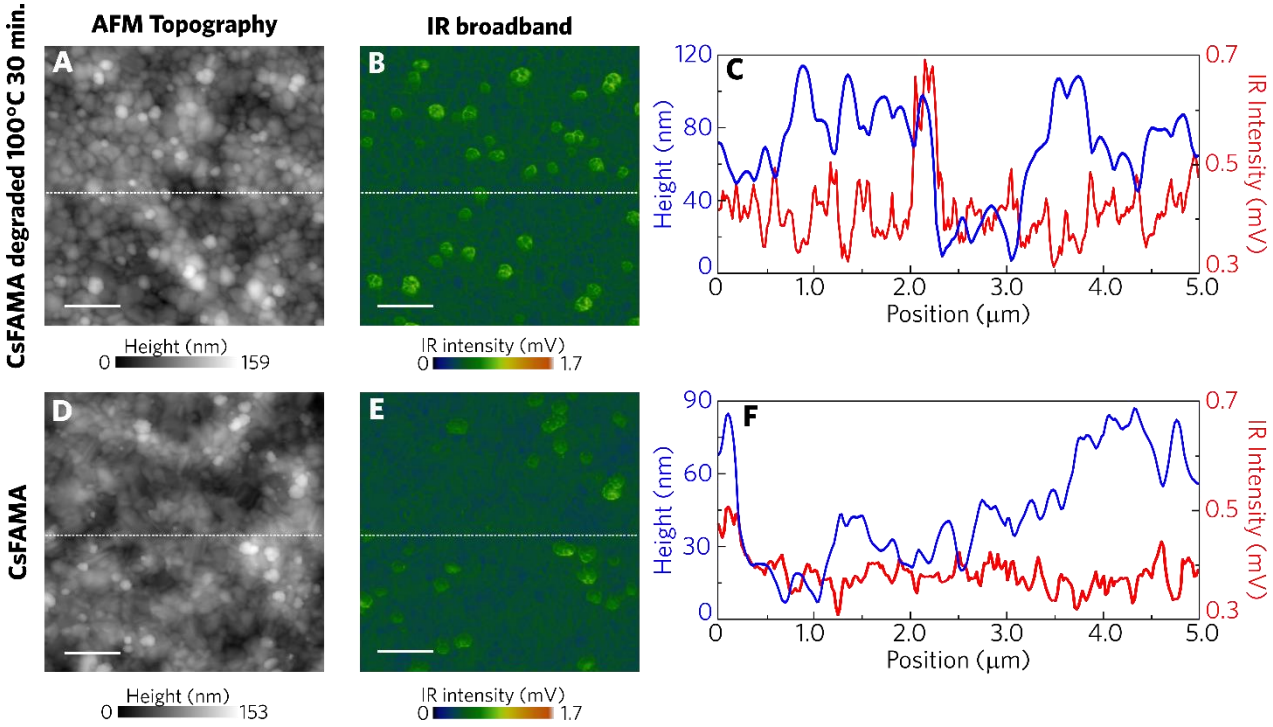

Fig. S3. Nano-FTIR of the intentionally degraded CsFAMA film at 100°C for 30 min. (**A**) Topography and (**B**) IR broadband of the CsFAMA sample heated at 100°C for 30 minutes. The degradation did not change significantly the topography of the sample compared with (**D, E**) CsFAMA fresh, neither the IR broadband. It can be observed in the IR broadband that vibrational activity increased at grain boundaries (**C, F**), as observed in the profiles along selected dashed lines. The enhanced activity has been attributed to the increase of the PbI_2 in the sample due to the MA depletion by heating.

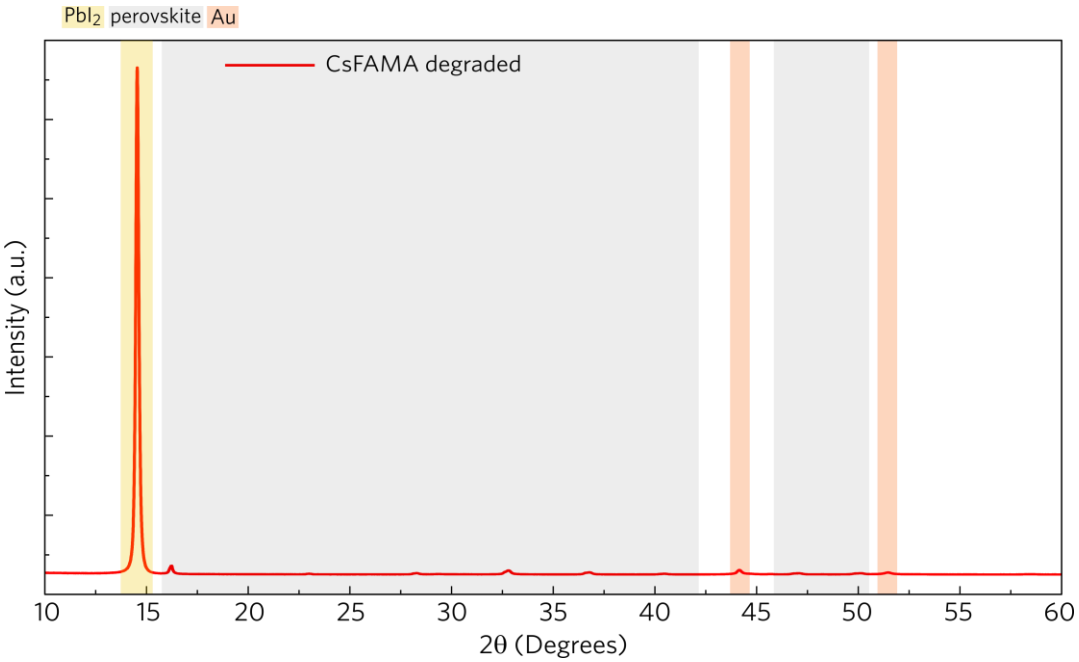

Fig. S4. High-resolution XRD pattern of the CsFAMA degraded perovskite sample deposited onto Si/Au substrate. The XRD pattern shows the main peak from PbI_2 and smaller peaks from perovskite. The mass fractions were estimated by Rietveld refinement to be 52% PbI_2 and 48% perovskite. The XRD peaks are displaced to higher 2θ because the measurements were carried out with 7 keV (λ = 1.541 Å).

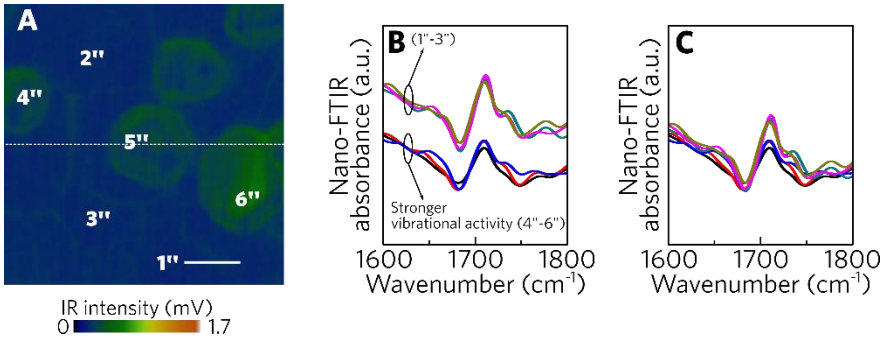

Fig. S5. Comparison between intensity of the spectra collected at different regions of the FAMA film. (**A**) IR broadband image of FAMA film. The points 1"-3" and 4"-6" represent the regions where the point spectra were collected in the smaller and higher IR intensity, respectively. The spectra are very similar in the same group (**B**) but the comparation (**C**) between these ones revealed that spectra at higher intensity presented smaller FA absorption than spectra at smaller IR activity regions.

Table S1. Film composition as obtained from Rietveld refinement using the software MAUD. A March–Dollase model for texture was used giving a degree of preferred orientation above 85% in the following crystallographic directions: Au (111), (Cs)FAMA (111) and PbI_2 (001).

	Mass fraction			Rwp
	Perovskite	PbI_2	Yellow phase	
CsFAMA	0.98(2)	0.01(1)	Background level	14%
CsFAMA degraded	0.48(8)	0.52(8)	Background level	17%
FAMA	0.78(5)	<0.01	0.22(5)	11%