

Supporting Information

Effective solvent-additive enhanced crystallization and coverage of absorber layers for high efficiency formamidinium perovskite solar cells

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Experimental

Materials and reagents

Lead iodide (PbI₂, 99%), lithium bis(trifluoromethylsulphonyl) imide (Li-TFSI, 99.95%), 4-tert-butylpyridine (tBP, 96%), and chlorobenzene (99.8%) were ordered from Sigma-Aldrich; CN from Alfa-Aesar; Hydroiodic acid (57 wt%) and formamidine acetate (99%) from the Tianjin Kermol Chemical Reagent Developing Center; 2,2,7,7-tetrakis-(N,N-di-p-methoxyphenyl-amine)-9,9-spirobiorene (spiro-MeOTAD) from YingkouYouxuan Technology Company; Fluorine-doped tin oxide (FTO) glass from Wuhan Geao Company. All materials were used without purification.

Materials synthesis and solar cell fabrication

To synthesize the FAI precursor, 30 mL of hydroiodic acid ($\geq 45\%$) solution and 15 mg of formamidine acetate were mixed in an ice bath for 2 h. The resulting solution was evaporated at 60 °C to remove solvents. The yellowish raw product was re-dissolved in methanol; recrystallized; washed using diethyl ether for three times; and finally dried at 60 °C in a vacuum oven for 24 h to harvest pure FAI crystals. The FAI and PbI₂ were mixed in 1:1 mole ratio in γ -butyrolactone (GBA) dimethyl sulfoxide (DMSO) ($V_{\text{GBA}}: V_{\text{DMSO}}=7:3$) at 70°C for 2 h. The different volume ratio of the CN solvent-additive was mixed in the above FAPbI₃ precursor solution. To prepare the

thin film coating, the precursor solution was spin-coated on the substrates at 4000 rpm for 30s in a glove box. The coating was then heated at 150°C for 30 min to allow the precursor fully converted into perovskite film. For the hole transport layer (HTL), 90 mg spiro-MeOTAD, 22.5 μ L Li-TFSI/acetonitrile (520 mg mL⁻¹) and 36 μ L 4-tert-butylpyridine were dissolved in 1 mL chlorobenzene to form the HTL precursor solution. It was applied by spin-coating it onto the FAPbI₃ film at 5000 rpm for 30 s. A 60 nm-thick Au was then deposited on the top of the HTL by thermal evaporation. The active cell area of 0.09 cm² was defined by the metallic mask used with the Au coating.

Measurements and characterization

The current-density voltage (J-V) performance of the solar cells were measured using a Keithley 2400 system under AM 1.5 at 100 mW cm⁻² light illumination. The power output of AM 1.5G Oriel solar simulator was calibrated by a NREL-traceable KG5 filtered silicon reference cell. The scan rate was 0.1 V s⁻¹, the scan step 0.02 V, and the scan delay time 50 ms. X-ray diffraction (XRD) was measured on a Rikagu diffractometer (Cu radiation, λ = 0.1546 nm) running at 40 kV and 30 mA. The absorbance spectra were measured using a PerkinElmer spectrophotometer (Lambda 950 UV-vis-NIR). Scanning electron microscopy (SEM) images were acquired using a Jeol JSM-6700F. The height atomic force microscopy (AFM) images were taken on a Bruker Metrology Nanoscope VIII AFM in ambient. The quantum efficiency (QE) measurements were performed to evaluate the spectral response of the fabricated solar cells by using (QTest Station 2000ADI system (Crowntech Inc.)) in AC mode.

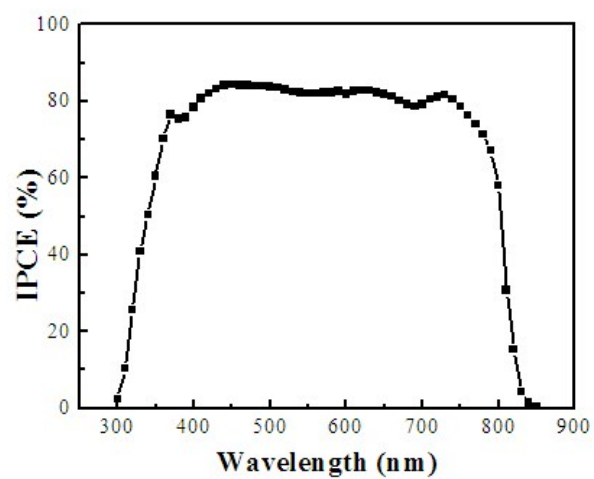


Figure S1 IPCE spectra of FAPbI₃ device with 1% CN solvent-additive, where the integrated J_{sc} was calculated to be 22.32 mA cm⁻² for FAPbI₃.

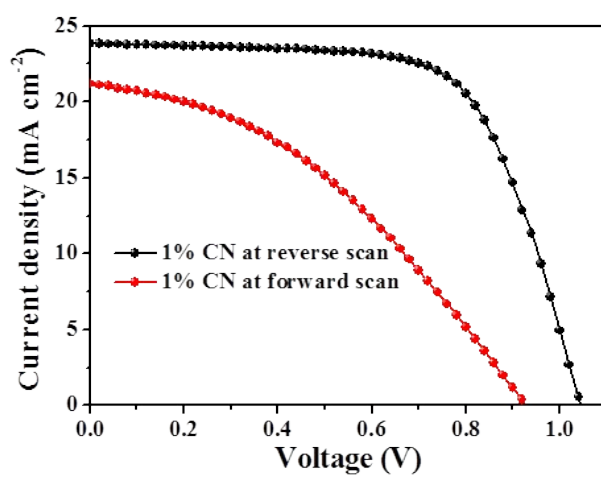


Figure S2 J-V characteristics of FAPbI₃ device with 1% CN solvent-additive respect to reverse and forward scan direction.

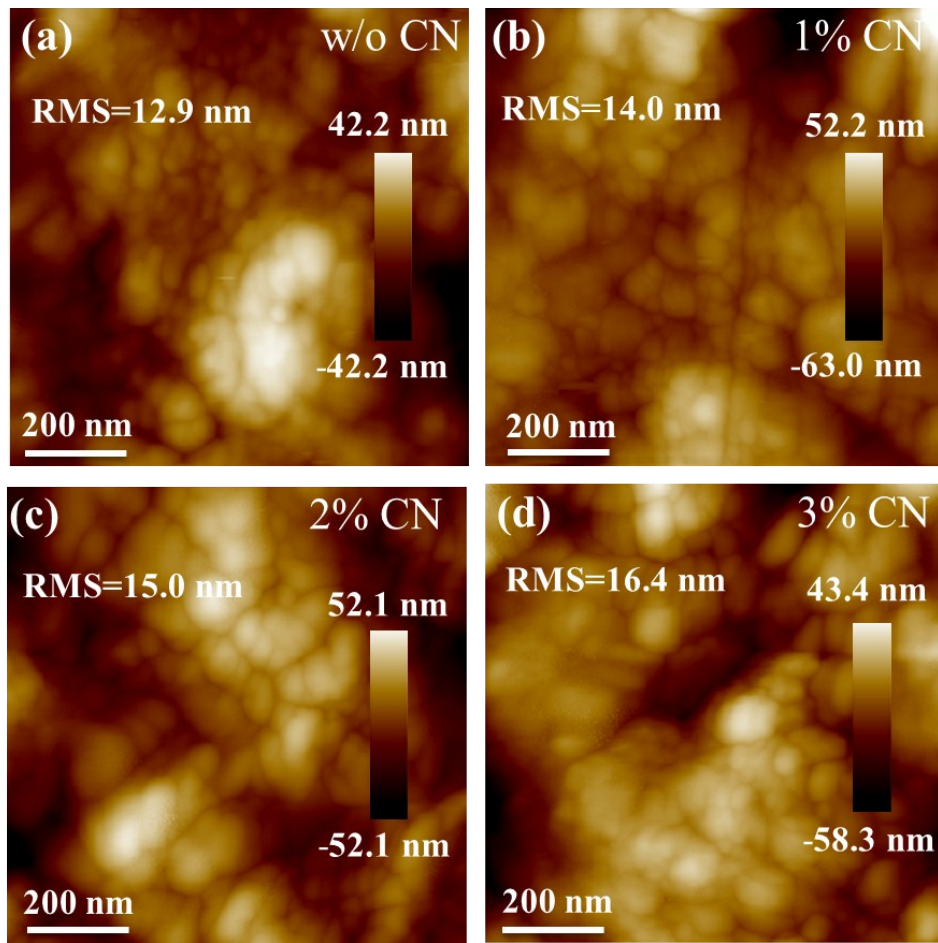


Figure S3 AFM height images of FAPbI₃ film without CN solvent-additive (a), and with 1% CN solvent-additive (b), 2% CN solvent-additive (c), 3% CN solvent-additive (d).

Table S1. The key parameters of devices based on 1% CN solvent-additive.

Sample	V _{oc} (V)	J _{sc} (mA cm ⁻²)	FF	PCE(%)
1	1.02	22.91	0.64	14.91
2	1.06	21.68	0.68	15.61
3	1.06	19.71	0.71	14.83
4	1.04	19.56	0.74	15.04
5	1.06	20.05	0.74	15.69
6	1.04	23.84	0.67	16.53
7	1.06	21.03	0.72	15.95
8	1.04	22.04	0.68	15.61
9	1.04	21.10	0.71	15.58
10	1.02	22.14	0.68	15.68
Average	1.04 ± 0.02	21.41 ± 1.40	0.70 ± 0.03	15.54 ± 0.51

Table S2. Fitting decay time of the FAPbI₃ films with different CN ratios.

Sample	τ_{ave} (ns)	τ_1 (ns)	Amplitude of τ_1 (%)	τ_2 (ns)	Amplitude of τ_2 (%)
0 %	77.29	1.5	42.36	78.36	57.64
1 %	87.15	2.72	47.57	89.48	52.43
2 %	155.19	8.88	36.81	159.94	63.19
3 %	176.44	8.52	43.21	182.42	56.79