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Building (001) Oriented $FAPbI_3$ Films for high-performing Perovskite Solar Cells

Yingke Ren[a], Hongyang Fu[a], Yingjie Sun[a], Zhaoqian Li[*b], Xinge Guo[*a] and Xingtao An[*a]

[a]*Hebei Key Laboratory of Photoelectric Control on Surface and Interface, College of Science, Hebei University of Science and Technology, Shijiazhuang 050018, China.*
[b]*Key Laboratory of Photovoltaic and Energy Conservation Materials, CAS, Institute of Solid State Physics, Hefei Institutes of Physical Science, Chinese Academy of Sciences, Hefei, Anhui, 230031, China.*

*Corresponding author

E-mail: zqli@rntek.cas.cn (Z Li)

E-mail: guo.xg2008@163.com (X Guo)

E-mail: anxt2005@163.com (X An)

EXPERIMENTAL SECTION

Film Fabrication (TiO_2)

Fluorine-doped tin oxide (FTO, Pilkington, TEC15) glass was etched with HCl aqueous and Zn powder. The obtained glass was then cleaned with detergent, distilled water and ethanol, respectively. The blocking TiO_2 layers (bl-TiO_2) were deposited on the as-prepared FTO though spray pyrolysis method followed by calcining at 510 °C for 30 min. The mesoporous TiO_2 (mp-TiO_2) films were deposited on the above bl-TiO_2 layer by means of spin-coating the TiO_2 paste (Dyesol 30NR-T). The obtained layers were following by heating at 510 °C for 20 min.

Film Fabrication (BA_2PbI_4)

The 2D BA_2PbI_4 perovskite precursor solution was prepared by dissolving BAI and PbI_2 at a molar ratio of 2:1 in a mixed solvent of DMF and DMSO at a volume ratio of 4:1 to form a solution of 1.3 M concentration. The as-prepared solutions were spin-coated onto the mp-TiO_2 layer at 1100 rpm for 20 s and 5000 rpm for 30 s at room temperature. Thereinto, in the second step (5000 rpm for 30 s), after spin-coating for 20 s, 0.75 ml chlorobenzen (CB) was quickly dripped on the center of the rotating substrate under the air flow.

Solution Processed $FAPbI_3$

To prepared $FAPbI_3$ layer, 40 μL solution of BAI (5mg/mL) dissolved in the IPA (1 mL) was dropped on the as prepared BA_2PbI_4 film (5000 rpm for 30 s). Subsequently, the as-prepared films were heated at 100 °C for 15 min.

Vapor Processed $FAPbI_3$

FAI powder was uniformly spread around the BA_2PbI_4 coated substrates in a Petri dish covered with a lid. The petri dish was placed in a vacuum oven (10 kPa) set at 150 °C for 6 hours. As prepared perovskite films were first washed with 2-propanol to remove the FAI residue.

Solar Cell Fabrications

The spiro-OMeTAD solution (25 μL), which consists 73 mg of spiro-OMeTAD, 28 μL of 4-tert-butyl pyridine and 17.5 μL of lithium bis (trifl uoromethanesulfonyl) imide (Li-TFSI) solution (520 mg of Li-TSFI in 1 mL of acetonitrile) in 1 mL of CBZ, was spin-coated on the perovskite film at 3000 rpm for 20 s. Finally, Au electrode

with a thickness of 60 nm was deposited by using thermal evaporation under vacuum at a constant evaporation rate of 0.6 nm s^{-1}.

Characterization

Field emission scanning electron microscope (SEM) was used to study the top-morphology of the prepared film (FEI Sirion 200, Netherland). The crystal phase was obtained with X-ray diffraction (XRD) using Cu Kα beam (X'Pert Pro, Netherland). The current-voltage curve was measured under one sun illumination (AM 1.5G) with a solar simulator (94043A, USA) equipped with Keithley 2400 source meter. XPS spectra were collected using a Thermo-Scientific Ka X-ray Photoemission Spectrometer operating at a base pressure of $5x10^{-8}$ mbar and using an Al anode at a power of 72 W, a hemispherical analyzer, and pass energy of 20 eV. No flood gun was used as all samples are fabricated on the FTO substrate with decent electrical conductance. Ultraviolet-visible (UV–vis) absorption spectroscopy was measured using the spectrophotometer (SOLID3700, Shimadzu Co. Ltd, Japan). Incident photon-to-electron conversion efficiency (IPCE) spectra were measured using a 300 W xenon lamp with a spectral resolution of 5 nm equipped with order sorting filters (Newport/Oriel). Steady PL, TRPL and confocal PL mapping were recorded with a laser confocal Raman spectrometer (Princeton Instruments, Acton Standard Series SP-2558) and a 405 nm laser (OBIS LX-405) using a home-built confocal microscope on a 10 × 10 μm^2 sample area.

Calculations

First-principles calculations are performed by using density functional theory (DFT) implemented in Vienna Ab-initio Simulation Package (VASP).[1] Projector augmented-

wave (PAW) pseudopotential is used to account ion-electron interactions.[2] The correlation and exchange terms are described using general gradient approximation (GGA) in the scheme of Perdew–Burke–Ernzerh (PBE) functional.[3] A DFT-D3 scheme proposed by Grimme is used to take into account dispersive forces.[4] During all calculations, the kinetic energy cut off of 500eV was used, and the convergence criteria for energy and force are 10^{-5} eV and 0.02 eV/Å, respectively. The first Brillouin Zone is sampled with a k-point mesh of 4×4×2 within the Monkhorst–Packing scheme.[5]

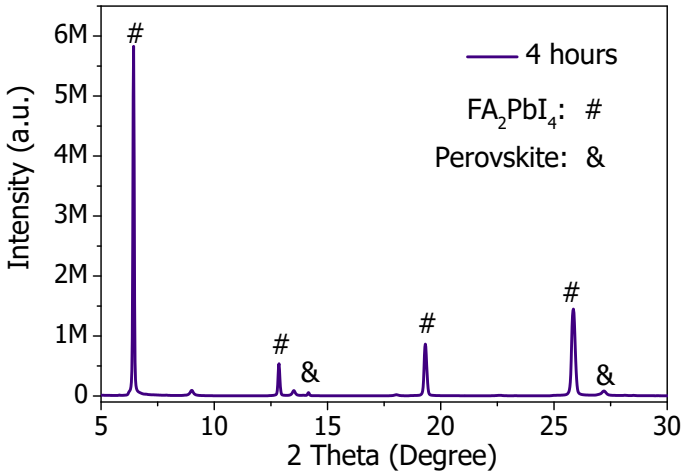

Figure S1 The FAI vapored process. XRD patterns of FAI vapor treated oriented template BA_2PbI_4 thin films for t=4 hours.

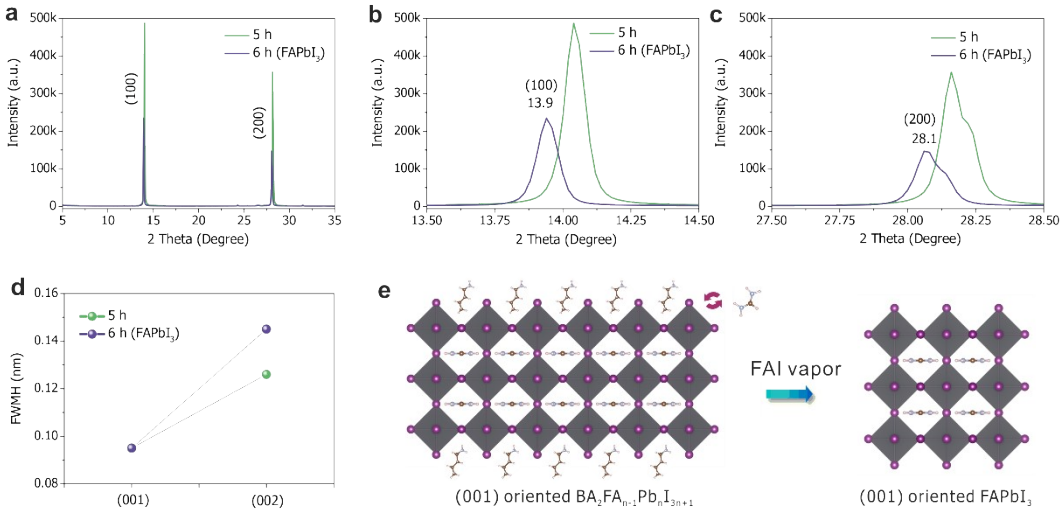

Figure S2 The FAI vapored process. (a-c) XRD patterns of FAI vapor treated oriented template BA_2PbI_4 thin films for t=5, 6 hours. (d) The XRD width of maximum heigh (FWMH) of corresponding perovskite layers. (e) Schematic of the FAI vapor reaction between oriented template $BA_2FA_{n-1}Pb_nI_{3n+1}$ and oriented (001) $FAPbI_3$.

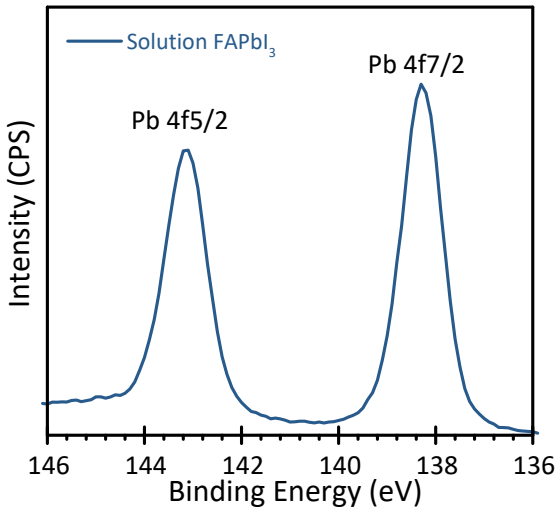

Figure S3 The FAI solution process. The Pb 4f XPS spectra of the $FAPbI_3$ based on FAI solution process.

Table S1 The optimized lattice constant for FA_2PbI_4. (a, b and c in the unit of Å, α, βand γin the unit of degree).

	a	9.43
	b	8.61
	c	20.68
α		94.92
β		75.38
γ		89.45