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Supporting Information for

A Practical Method for Fabricating PSCs with Superb Water Resistance via Additive Engineering

*Guanqun Feng[ab], Xiaochen Guo[ab], Faming Li[ab], Yulong Liao[a], Yuting Hou[ab], and Mingzhen Liu[*ab]*

a. Center for Applied Chemistry, University of Electronic Science and Technology of China, Chengdu 611731, P.R. China.

b. School of Materials and Energy, University of Electronic Science and Technology of China, Chengdu 611731, P.R. China.

AUTHOR INFORMATION

Corresponding Author

* E-mail: mingzhen.liu@uestc.edu.cn

Experimental Section

1.Materials: All the solid chemicals were used without purification, including MAI (99%, DYESOL), PbI_2 (99%, Sigma-Aldrich), 2-aminoethanethiol hydrochloride (2-AET·HCl, 98%, Aladdin), Spiro-OMeTAD (99.8%, Borun Chemicals), Li-TFSI (Sigma-Aldrich). The dehydrated solvent includes N,N-dimethylfrmamide (DMF, 99.8%, Sigma-Aldrich), Dimethyl sulfoxide(DMSO, 99.8%, Sigma-Aldrich), chlorobenzene (99.8%, Sigma-Aldrich) and acetonitrile(99%, J&K Chemical)

2.Preparation of $Cs_xMA_{(1-x)}PbI_3$·(0.68(1-x))2-AET·HCl precursor:

$MAPbI_3$·(0.68)2-AET·HCl precursor: 461 mg PbI_2, 159 mg MAI and 77 mg 2-AET·HCl were mixed in 0.63 ml DMF.

$CsPbI_3$ precursor: 461 mg PbI_2 and 260 mg of CsI were completely dissolved in 2 ml DMF.

$Cs_xMA_{(1-x)}PbI_3$·(0.68(1-x))2-AET precursor : $MAPbI_3$·(0.68)2-AET·HCl precursor and $CsPbI_3$ precursor were mixed in proportion as shown in Table S1.

Table S1. Details for precursor of $Cs_xMA_{(1-x)}PbI_3$·(0.68(1-x))2-AET·HCl

x value	$CsPbI_3$ precursor/μL	$MAPbI_3$·2-AET·HCl precursor/μL
0.00	0	2000
0.05	100	1900
0.10	200	1800
0.15	300	1700
0.20	400	1600
0.25	500	1500
0.30	600	1400

3.Device Fabrication: Glass substrates were cleaned in following order: detergent for 10 min, acetone for 30 min, ethyl alcohol for 30 min and oxygen plasma for 10 min. The compact TiO_2 and mesoporous TiO_2 were both deposited by spin coating at a spin speed of 4200 rpm for 30 sec on the cleaned glass substrate, and then annealed at 500℃ for 30min. The fully dissolved precursor solution was spin-coated on the mp-TiO_2 layer at 3500 rpm for 10 sec then 6000 rpm for 20 sec, followed by a thermal annealing at

100°C for 10 min and 150 °C for 2 min, aimed to obtain a dense $Cs_xMA_{(1-x)}PbI_3$·(0.68(1-x))2-AET film. The hole-transporting layer was then deposited via spin-coating as reported.[1] Au electrode was vapored at a constant rate of 0.2 nm/s.

4.Characterization: Absorption measurements were operated at room temperature through UV-vis spectrophotometer (PerkinElmer Lamuda 365). The PL measurements were performed using a Renishaw in Via Raman Microscope (UK) using a 485 nm laser as excitation source. X-ray diffraction (XRD) was executed with a Bruker D8 Advance diffractometer using Cu Kα1/2 source and Vantec-1 detector in 2θ-Omega model. The morphology of perovskite films are investigated through a SEM (Inspect FEI) at an accelerating voltage of 10kV. Thermal gravimetric analysis (TGA-Q50, TA Instrument) was used to study the thermal stability, under nitrogen atmosphere at a heating rate of 20°C/min from room temperature to 500°C. Current-voltage (JV) curves were collected by using a Keithley 2400 source meter under simulated AM 1.5G solar illumination (Newport ORIEL Sol 3A) from a xenon lamp whose power output was calibrated by a standard reference of a Newport silicon solar cell. The active area is 0.09 cm^2. The J-V curves were measured via reverse scanning at scan rate of 45 mV/s.

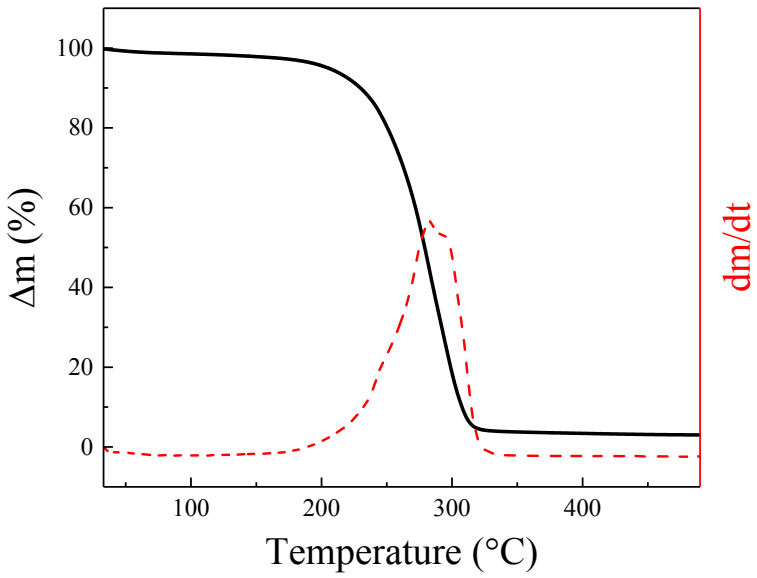

Figure S1: Thermal gravimetric analysis and differential thermal analysis curve of 2-AET·HCl

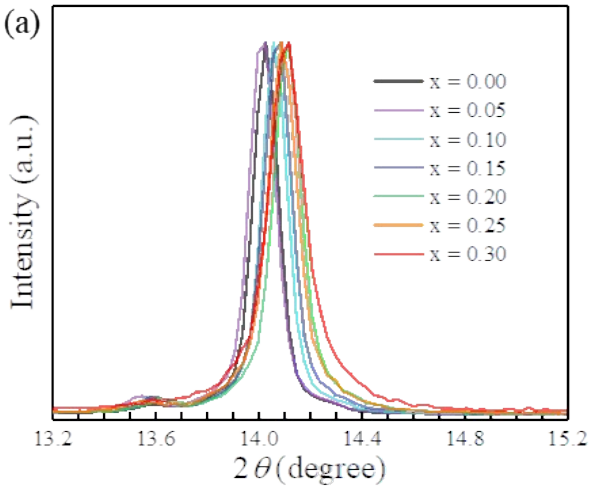

Figure S2: XRD patterns of $Cs_xMA_{(1-x)}$ PbI_3·(0.68(1-x))2-AET where x equals to 0.00, 0.05, 0.10, 0.15, 0.20, 0.25, 0.30.

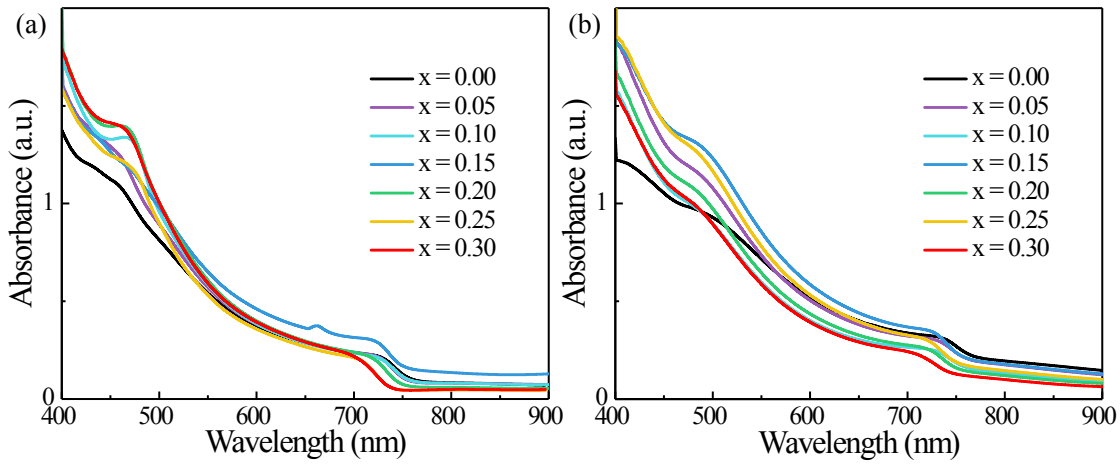

Figure S3: Absorption spectra of $Cs_xMA_{(1-x)}$ PbI_3·(0.68(1-x))2-AET before (a) and after (b) water immersion for 10 seconds, where x equals to 0.00, 0.05, 0.10, 0.15, 0.20, 0.25, 0.30.

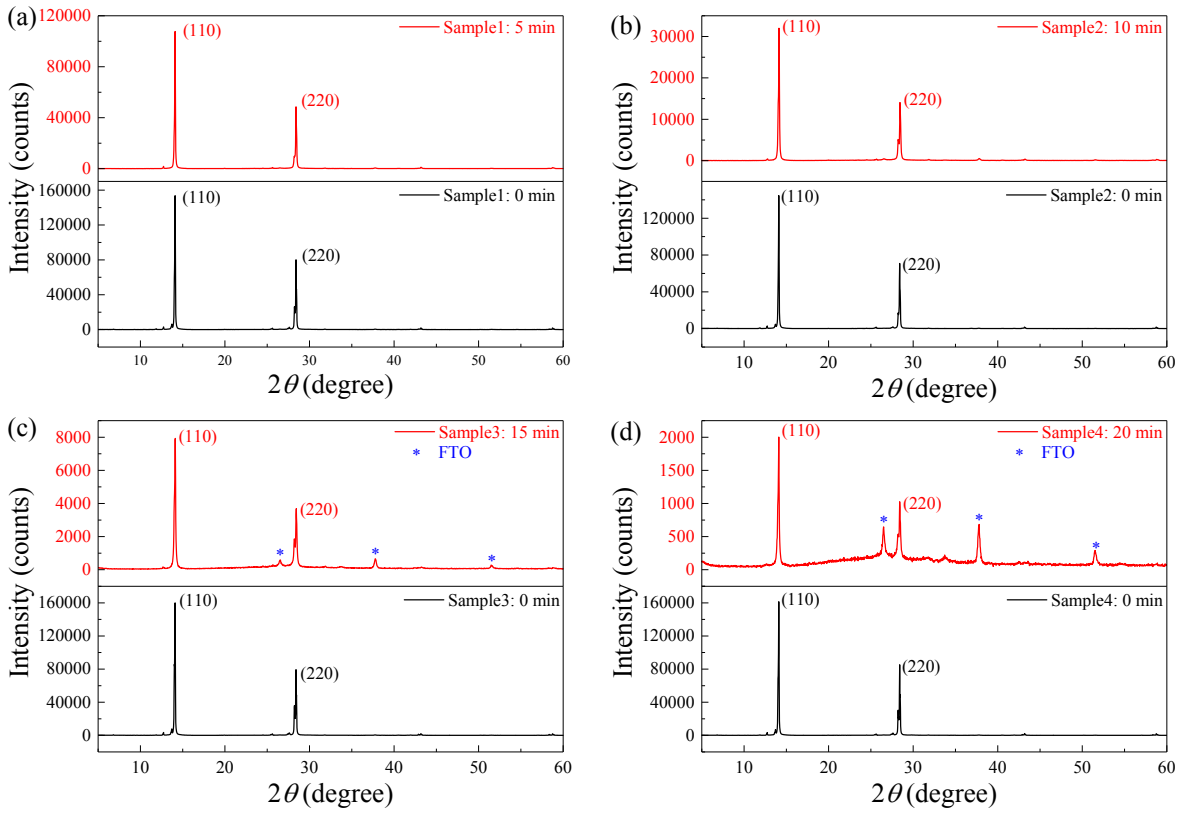

Figure S4: XRD patterns of perovskite films before and after immersing in water for varied times

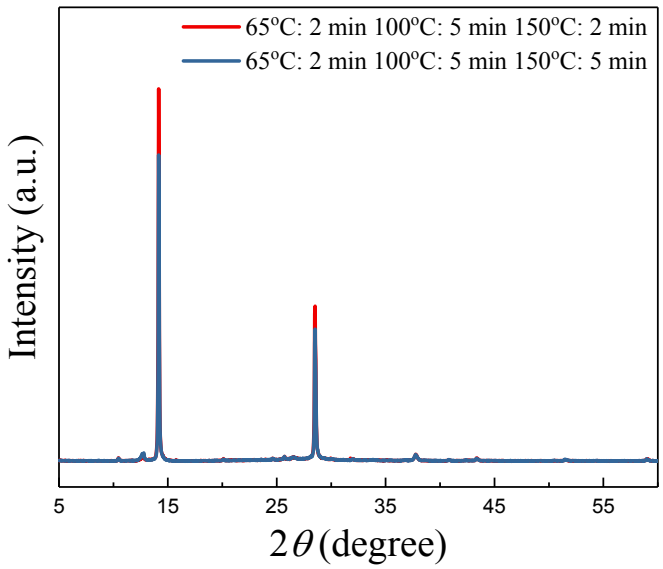

Figure S5: XRD patterns of perovskite films annealed at 65°C, 100°C and 150°C by steps with varied annealing times at 150 °C

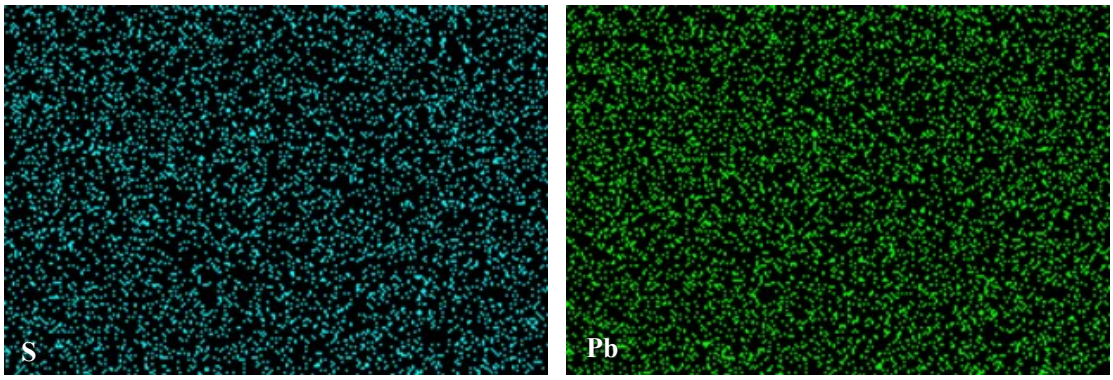

Figure S6: Energy dispersive X-ray spectrum of S and Pb element.

Reference:

(1) Li, F.; Zhu, W.; Bao, C.; Yu, T.; Wang, Y.; Zhou, X.; Zou, Z., Laser-assisted crystallization of $CH_3NH_3PbI_3$ films for efficient perovskite solar cells with a high open-circuit voltage. *Chem. Commun.,* **2016**, 52 (31), 5394-5397.