Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.
This journal is © the Owner Societies 2023

Supporting Information

In-Situ Surface Regulation of 3D Perovskite Using Diethylammonium Iodide for High-efficient Perovskite Solar Cells

Xiaopeng Yue[1,2‡], *Yingying Yang*[1‡], *Xing Zhao*[1], *Bingbing Fan*[1], *Huilin Yan*[1], *Shujie Qu*[1], *Qiang Zhang*[1], *Zhineng Lan*[1], *Shuxian Du*[1], *Hao Huang*[1], *Luyao Yan*[1], *Xinxin Wang*[1], *Peng Cui*[1], *Junfeng Ma*[1], *Meicheng Li*[1]*

[1]State Key Laboratory of Alternate Electrical Power System with Renewable Energy Sources, School of New Energy, North China Electric Power University, Beijing 102206, China

[2]School of Energy and Environmental Engineering, Hebei University of Engineering, Handan, Hebei 056038, China

*Corresponding authors：

E-mails: mcli@ncepu.edu.cn (*Meicheng Li)*

Experimental details

Materials. Diethylammonium iodide (DAI) was purchased from Tokyo Chemical Industry (TCI). PbI_2 was purchased from Thermo scientific. Titanium tetrachloride ($TiCl_4$,) was purchased from Aladdin. Formamidinium iodide ($CH(NH_2)_2)I$, FAI), cesium iodide (CsI), methylammonium chloride (CH_3NH_3Cl, MACl), 4-tert-butylpyridine (tBP), li-bis(trifluoromethanesulfonyl)imid (LI-TFSI) and 2,2′,7,7′-Tetrakis[N,N-di(4-methoxy phenyl)amino]-9,9′-spirobifluorene (spiro-OMeTAD) were purchased from Xi'an Polymer Light Technology Corporation. N, N dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and chlorobenzene (CB) were purchased from Acros. Isopropanol (IPA) and acetonitrile (ACN) were purchased from Sigma-Aldrich. All chemicals were used without further purification. FTO glass (12 × 18 mm, 8 $\Omega \cdot sq^{-1}$) was purchased from Youxuan New Energy Technology Co. LTD (Yingkou, China). Anhydrous ether was purchased from Tianjin Jindongtianzheng Precision Chemical Reagent Factory.

Solution Preparation. TiO_2 precursor solution was prepared by diluting 3 mL $TiCl_4$ precursor with 150 mL deionized water. The perovskite precursor solution was prepared by dissolving PbI_2 (0.7420 g), FAI (0.2244 g), MACl (0.0101 g) and CsI (0.0198 g) in 1 mL DMF and DMSO (v:v=4:1). DAI was dissolved in IPA with varied weight concentrations. The spiro-OMeTAD solution was prepared by mixing 72.3 mg spiro-OMeTAD, 27 μL 4-tBP and 17.5 μL Li-TFSI solution (520 $mg \cdot mL^{-1}$, in ACN) in 1 mL CB.

Device Fabrication. All devices were deposited on FTO glass substrates, which were cleaned sequentially in detergent, ethanol and water for 15 min and then dried with nitrogen. Transparent TiO_2 films were prepared as electron transport layer by chemical bath method that $TiCl_4$ precursor solution is water-bathed at 70 °C for 40 minutes. Then the as-prepared FTO/TiO_2 films were rinsed with water and blown with dry N_2 for later use. The perovskite precursor was spin-coated on FTO/TiO_2 in N_2 glove box at 4000 rpm for 18 s. At 5 s after the spin-coating, 900 μL ether was dropped onto the substrate to accelerate the crystallization process, followed by annealing at 110 °C for 60 min in air to promote the crystallization of perovskite. DAI/IPA with different concentrations were spin-coated at 4000 rpm for 30s, followed by annealing at 100 °C for 3 min. The spiro-OMeTAD solution was deposited by spin-coating at 4000 rpm for 30 s without further annealing. Metal electrode (70 nm Au) was deposited on the hole transporting layer using a thermal evaporator to accomplish the solar cell fabrication.

Characterization. FTIR spectra was measured by Bruker INVENIO. XPS spectra was characterized by Thermo Fisher Scientific ESCALAB 250Xi system equipped with Al K_α radiation. The morphologies of perovskite films were investigated using HITACHI SU8010 at an accelerating voltage of 5 kV and atomic force microscopy (FMNanoview 1000). The XRD patterns of the prepared films were measured using a Rigaku Ultima IV X-ray diffractometer with Cu Ka1(1.54Å). UV-visible absorption spectra were measured using a Shimadzu UV-2600 spectrophotometer. Steady-state and the time-resolved photoluminescence were performed by a FLS980 fluorescence spectrometer (Edinburgh Instrument) equipped with a 450 W Xe lamp and a picosecond-pulsed diode 405 nm laser (EPL-405). The GIWAXS measurements were conducted by Rigaku MicroMax-007HF equipped with a DECTRIS PILATUS3 R detector under the incident angle of 0.5°.

The current density-voltage (*J-V*) characteristics were measured using a source meter (Keithley 2400) under AM 1.5G irradiation with a power density of 100 $\mathrm{mW \cdot cm^{-2}}$ from a solar simulator (XES-301S + EL-100). The light intensity was calibrated with a standard silicon cell (the KG-5 reference cell). The external quantum efficiency (EQE) was measured using QE-R systems (Enli Tech. Hsinchu Taiwan China) under AC mode, the light intensity was adjusted by the standard single-crystal Si photovoltaic cells before the measurement. The electrochemical impedance spectroscopy (EIS) of PSCs were analyzed using a Zahner-Zennium electrochemical workstation.

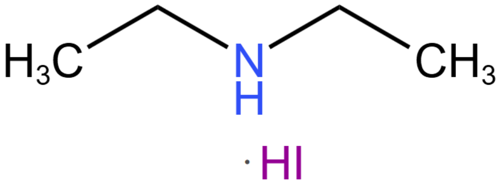

Figure S1. Molecular structure of DAI.

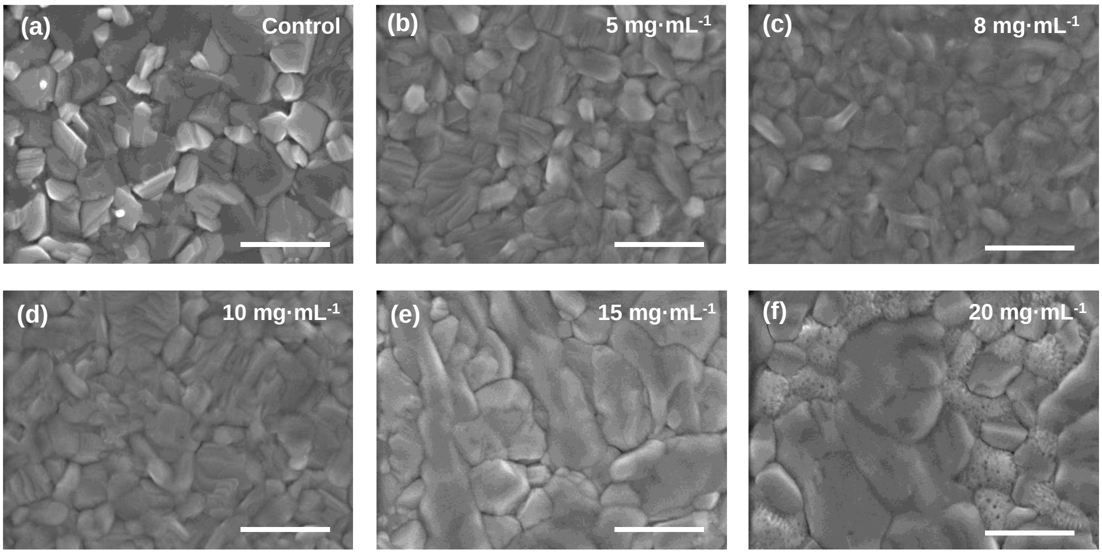

Figure S2. Top-view SEM images of perovskite films without and with different concentrations DAI treatment. a) Control; b) 5 mg·mL^{-1}; c) 8 mg·mL^{-1}; d) 10 mg·mL^{-1}; e) 15 mg·mL^{-1}; and f) 20 mg·mL^{-1}. Scale bars represent 1μm.

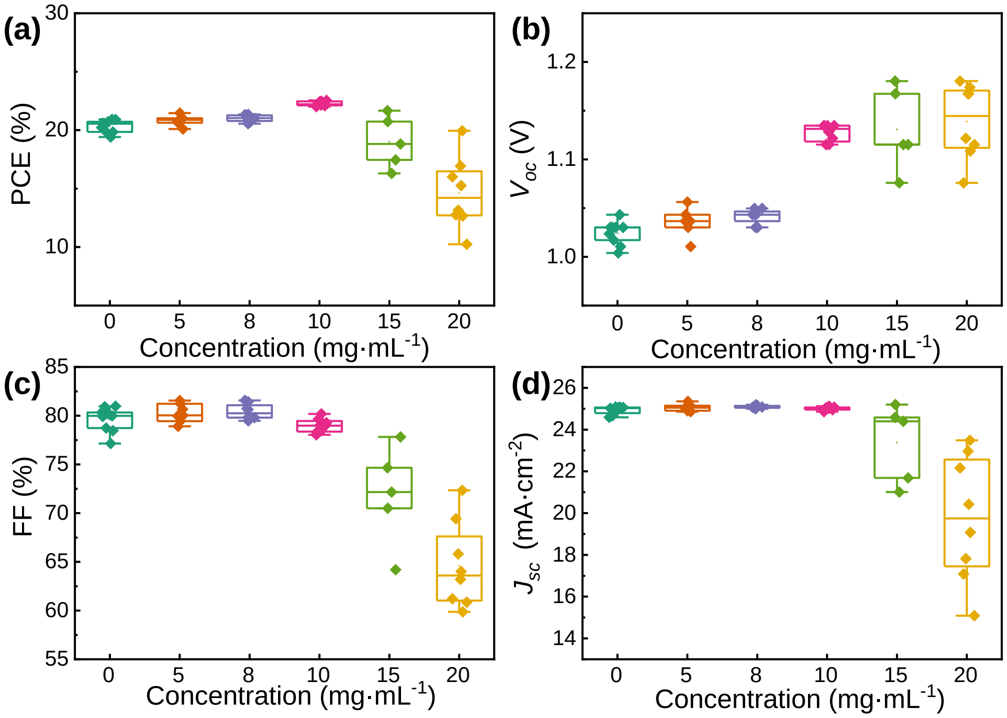

Figure S3. Statistical distributions of a) PCE; b) V_{oc}; c) FF; and d) J_{sc} of devices with different concentrations DAI treatment.

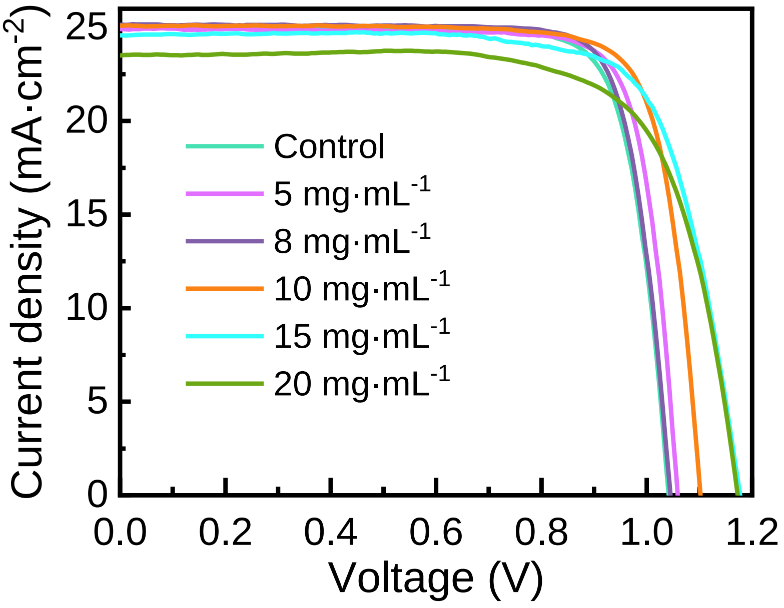

Figure S4. *J-V* curves of the best device for different concentration DAI treatment.

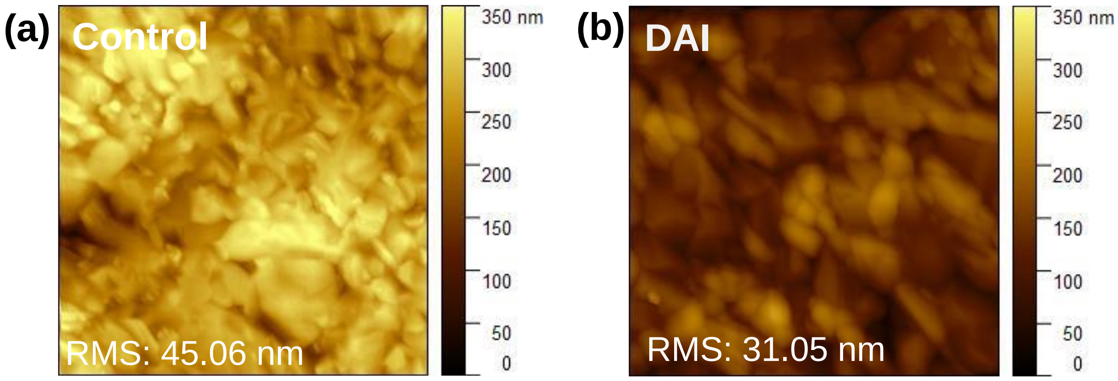

Figure S5. AFM height images (5 × 5 µm) of the a) control and b) DAI treated perovskite films.

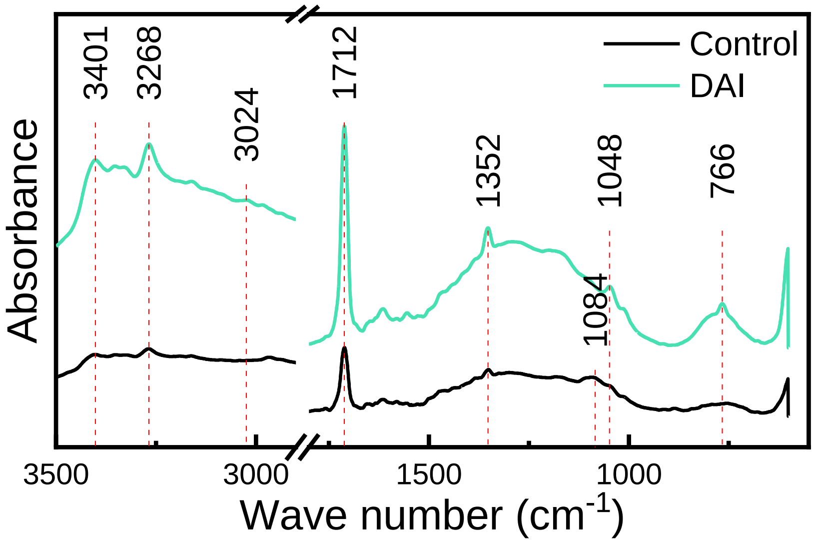

Figure S6. FTIR-ATR spectra of control and DAI-treated perovskite films.

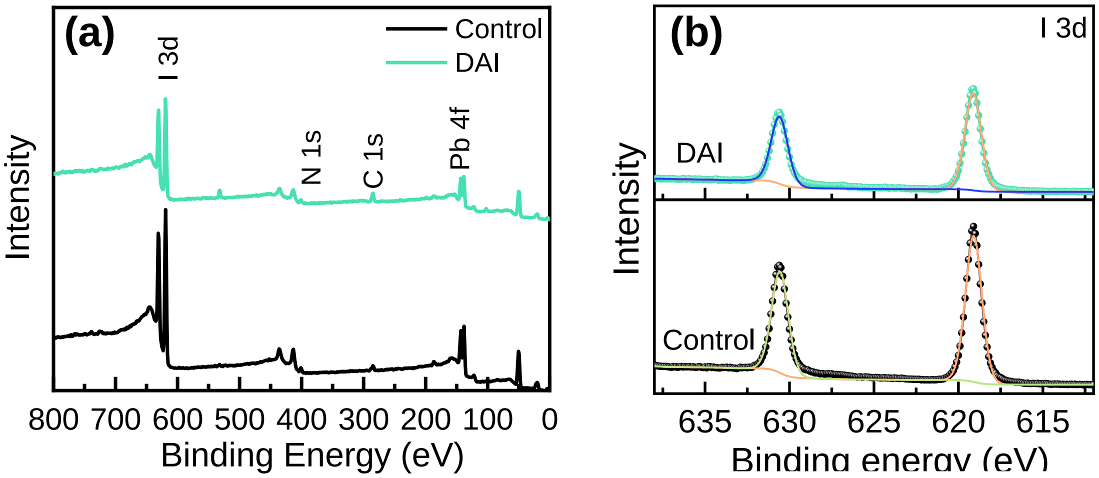

Figure S7. (a) the survey XPS spectra and (b) High-resolution XPS spectra of I 3d.

Table S1: Lifetime parameters of perovskite films treated with and without DAI, achieved by fitting the TRPL curves according to the biexponential equation, where the average lifetime $\tau_{average}$ are calculated according to the formula of $\tau average = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$.

	A_1	**τ_1 (μs)**	**A_2**	**τ_2 (μs)**	**$\tau_{average}$ (μs)**
Control	0.14	0.23	0.84	1.64	1.61
DAI	0.09	0.27	0.89	1.77	1.75

Table S2: EIS parameters of the PSCs with and without DAI treatment.

	R_s（Ω）	**CPE-T**	**CPE-P**	**R_{rec}（Ω）**
Control	19.24	6.38×10^{-8}	1.06	208
DAI	18.22	3.35×10^{-8}	0.96	772