Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information for

Twofold interfacial electric-field strategy: Boosting performance of electron transport layer-free perovskite solar cells with low-cost and versatile inorganic acid treatment

Hui Duan[1], Xin Li[1], Yue Gou[1], Haoyan Wang[1], Lin Fan[1, 2, 3], Yanli Chen[1, 2, 3], Jinghai Yang[1, 2, 3], Lili Yang[1, 2, 3]*, Fengyou Wang[1, 2, 3]*

1. Key Laboratory of Functional Materials Physics and Chemistry of the Ministry of Education, Jilin Normal University, Changchun 130103, China
2. National Demonstration Center for Experimental Physics Education, Jilin Normal University, Siping 136000, China
3. Key Laboratory of Preparation and Application of Environmental Friendly Materials, Ministry of Education, Jilin Normal University, Changchun 130103, China

Corresponding author:

Lili Yang, e-mail address: llyang1980@126.com

Fengyou Wang, e-mail address: *wfy@jlnu.edu.cn*

Illustration for Fig. S1: In order to determine whether new products were formed, we treated the ITO for a long time (60 min). Without any cleaning, we measured its X-ray diffraction (XRD). A new diffraction peak appears at 14.8°, which is assigned to the $In(PO_3)_3$.

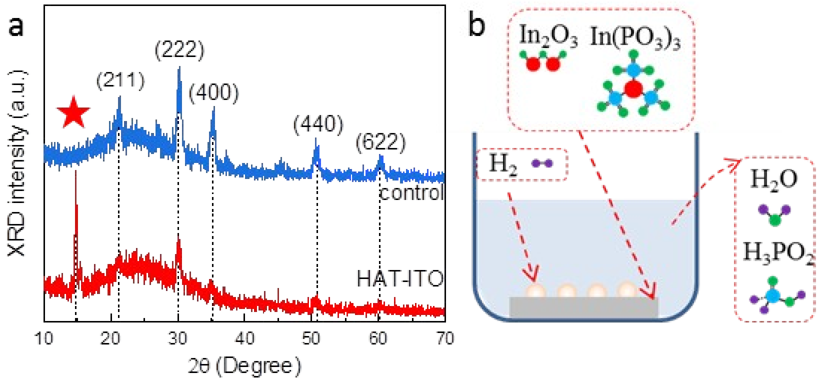


Fig. S1 (a) XRD patterns of the control-ITO, the HAT-ITO (processed for 60 min without any cleaning). (b) Schematic diagram of the experimental state after H_3PO_2 reacts with ITO for 60 minutes.

$$5In_2O_3 + 6H_3PO_2 \rightarrow 8In + 2In(PO_3)_3 + 9H_2O$$

$$2In + 6H_3PO_2 + 6H_2O \rightarrow 2In(PO_3)_3 + 15H_2$$

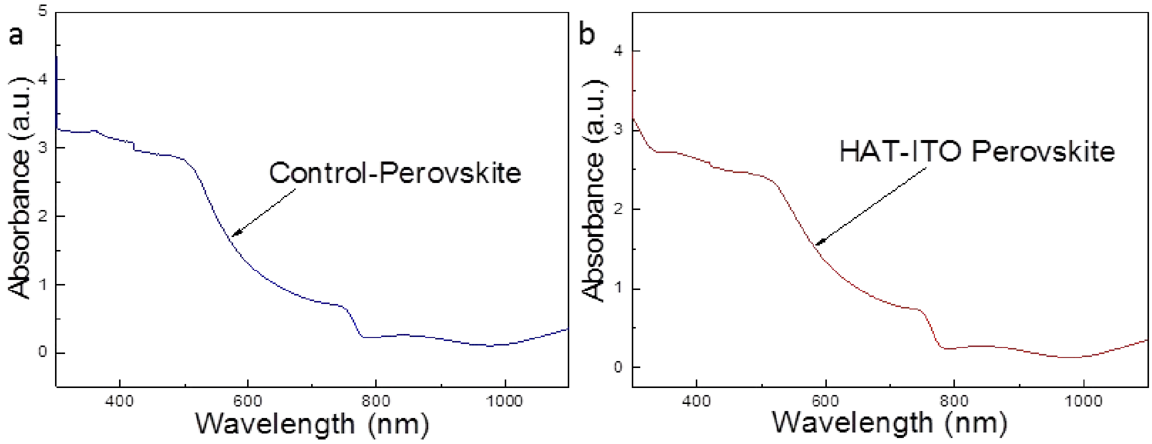


Fig. S2 UV-vis absorbance spectrum of (a) the control-ITO-perovskite and (b) the HAT-ITO-perovskite films.

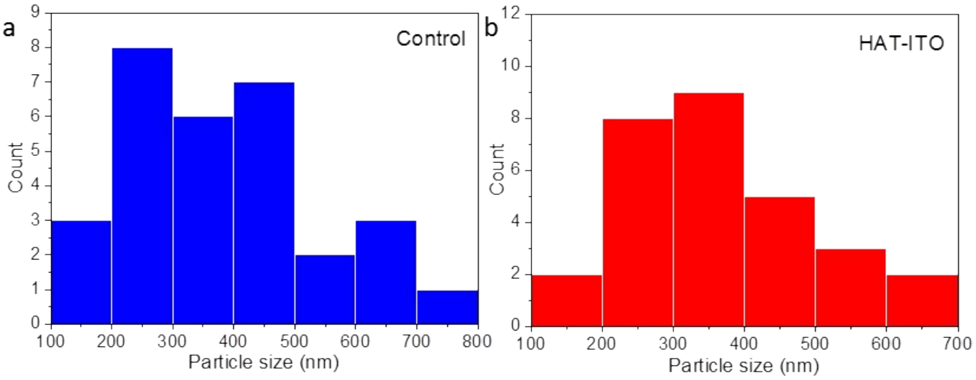
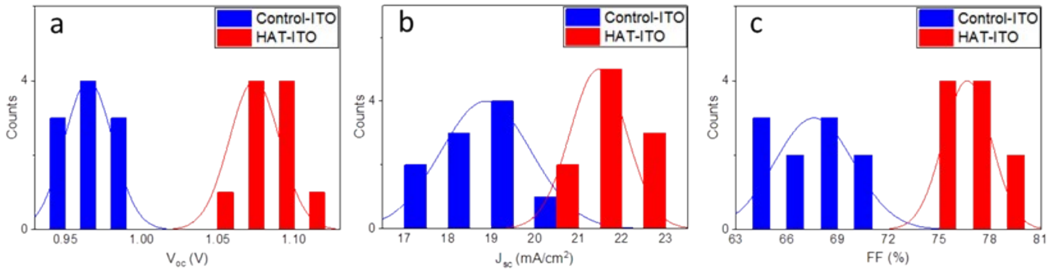


Fig. S3 The corresponding grain size distribution of (a) the control-ITO-perovskite and (b) the HAT-ITO-perovskite films.



.

Fig. S4 Histograms of (a) V_{oc} (b) J_{sc} and (c) FF with PSCs calculated from each of the 20 devices (10 devices of control-ITO and 10 devices with HAT-ITO).

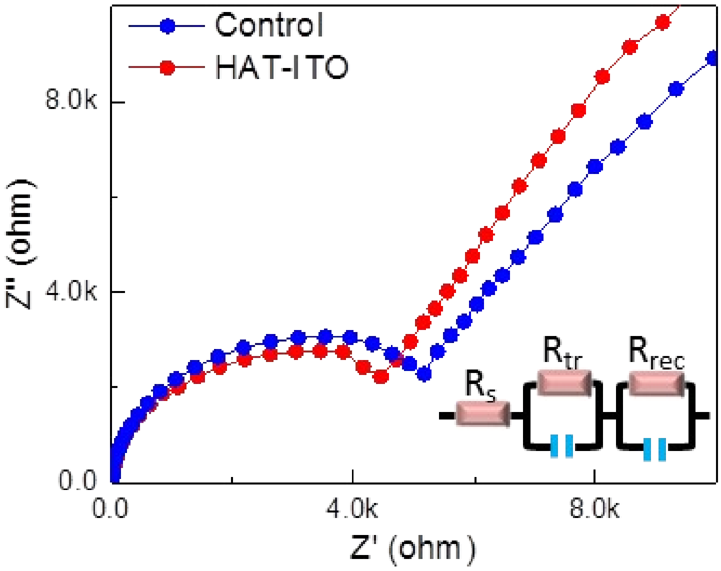


Fig. S5 Nyquist plots of (a) the control-ITO-device and (b) the HAT-ITO-device under dark condition. Inset c: The equivalent circuit used to fit the data.

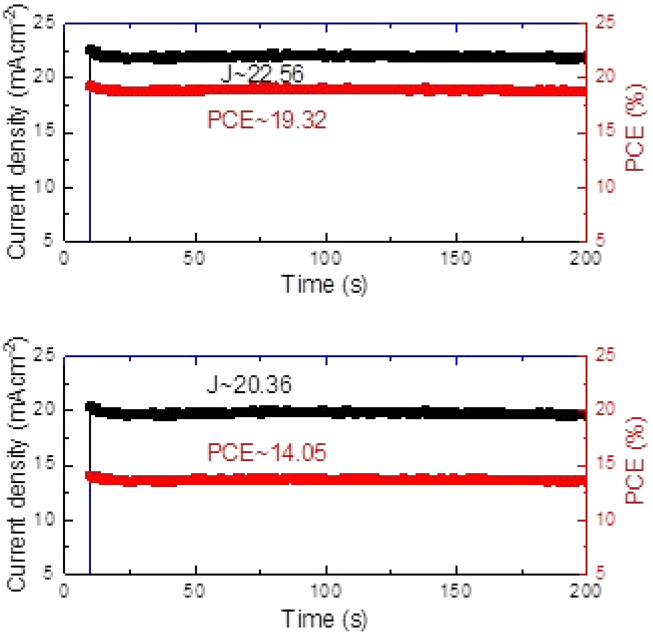


Fig. S6 (a) The control-ITO-device and (b) the HAT-ITO-device for the stabilized at V_{mpp} and current density.

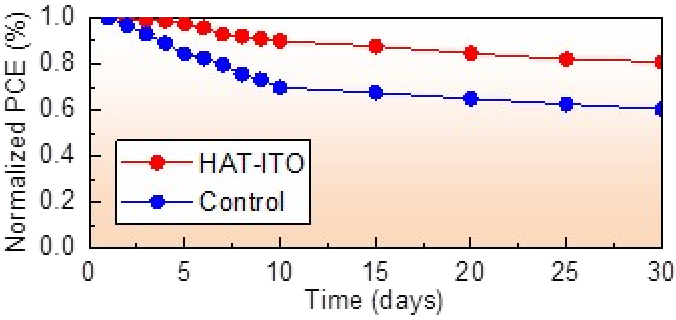


Fig. S7 The relationship between the device efficiency and storage time in the surrounding environment (~30 % humidity, T = 25 ^oC).

Table S1. TRPL lifetimes of the control-ITO-perovskite and the HAT-ITO-perovskite films

Sample	y_0	A_1	t_1 (ns)	A_2	t_2 (ns)
Control-ITO	0.0059	0.7457	8.5646	0.1844	155.57
HAT-ITO	0.0026	0. 5805	4.5207	0.415	103.7

Supplementary Note 1

Materials: Indium tin oxide (ITO) glass substrates, lead iodide (PbI_2), Methylammonium iodide (CH_3NH_3I, MAI), 4-tert-butypyridine and lithium bis (trifluoromethanesulfonyl) imide (Li-TFSI), mesoporous titania gel (Dyesol 18NR-T), 2,2′,7,7′-tetrakis (N,N-dip-methoxyphenylamine) 9,9′ Spirobifluorene (Spiro-OMeTAD) and all anhydrous solvents were purchased from YOUXUAN Technology Co. Ltd. (China). All chemicals and reagents were used as received from chemical companies without any further purification. The hypophosphorous acid was purchaused from Sinopharm Chemical Reagent Co., Ltd.

Supplementary Note 2

Fabrication of perovskite solar cells: Firstly, the ITO glass substrate was sonicated with deionized water, ethyl alcohol and acetone for 20 min then washed with UV-ozone for 20 min. Then we use H_3PO_2 solution to immerse the pre-cleaned ITO glass with at room temperature to form the HAT-ITO. 163 mg of MAI and 462 mg of PbI_2 were dissolved in a mixed solvent of Dimethylformamide (DMF) and Dimethyl sulfoxide (DMSO) (v: v = 3:7). The 90 mL of the mixture was deposited onto the HAT-ITO layer, i.e., 550 RPM for 10 s and 4000 RPM for 30 s to form $MAPbI_3$ films. Subsequently, the obtained films were dried at 100 ℃ for 10 min. Then, HTLs was prepared by mixing 72.3 mg of Spiro-OMeTAD, 28.5 mL with a solution of 500 mg/mL Li-TFSI in acetonitrile and 18.5 mL of 4-tert-butylpyridine in 1 mL of chlorobenzene. The 80 mL of the mixture solution was spin-coated on the prepared $MAPbI_3$ films at 3000 RPM for 30 s. Finally, the silver counter electrode is deposited over the film by thermal evaporation.

Supplementary Note 3

Characterization: The scanning electron microscope (SEM) images were taken using a Hitachi S-4800. The crystal structure of the $MAPbI_3$ films was carried out by X-ray power diffraction (XRD) (Japan Rigaku D/max-ga X-ray diffractometer) using Cu Kα (λ = 0.15406 nm) source. *J-V* was carried out under AM 1.5 G simulated sunlight illuminations (100 mW/cm^2, Model 94043A, Oriel). The spectral responses were obtained from an EQE measurement system (QEX10, PV measurement). The optical transmittance spectra were measured using a UV-5800PC Spectrophotometer integrated UV-Vis-near-infrared (NIR) spectrophotometer over a wavelength range of 300~1100 nm at the room temperature conditions. Electron-only devices (HAT-ITO/perovskites/Spiro-OMeTAD/Ag) were fabricated to calculate the trap state density of the devices. The defect density was determined by the equation for the trap-filled limit voltage. PL spectra were obtained using a PL microscopic spectrometer (Fluorolog-3 spectrometer, Horiba Jobin Yvon, America) with a 405 nm CW laser excitation source. The TRPL (Fluorolog-3 spectrometer, Horiba Jobin Yvon, America) were measured by using an emission wavelength of 770 nm. Electrical impedance spectroscopy (EIS) was performed by using the electrochemical workstation (CHI660C, Chen Hua, China) with the frequency range from 10 Hz to 0.1MHz in the dark.

Supplementary Note 4.

Calculation of the N_t

The linear correlation (orange) reveals an ohmic-type response at low bias voltage, when the bias voltage is above the kink point, which defines as the trap-filled limit voltage (V_{TFL}), the current nonlinearly increases (blue), indicating that the traps are completely filled. The trap density (N_t) can be obtained by

$$N_t = \frac{2\varepsilon_0 \varepsilon V_{TFT}}{eL^2}$$

where ε_0 is the vacuum permittivity, ε is the relative dielectric constant of $MAPbI_3$, e is the electron charge, and L is the thickness of the film.