## **Electronic Supplementary Information**

## Facile fabrication of highly efficient ETL-free perovskite solar cells with 20% efficiency by defect passivation and interface engineering

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## **Experimental Details**

FTO glass sheets (Nippon) were sequentially cleaned with detergent (Micro-90, 2% in water), acetone, ethanol and DI water for 30 min. TMAH (0.25% in water, Aladdin) was spincoated onto the FTO at 2000 rpm for 30 s. The TMAH treated substrates were then dried at 120°C for 3 min to remove any residual water. Perovskite precursor solution with a composition of FA0.75MA0.25PbI2.5Br0.5 was prepared by mixing stoichiometric ratio of CH<sub>3</sub>NH<sub>3</sub>I (MAI, Dyesol), NH<sub>2</sub>CH=NH<sub>2</sub>I (FAI, Dyesol), CH<sub>3</sub>NH<sub>3</sub>Br (MABr, Dyesol), PbI<sub>2</sub> (99.9985%, Alfa Aesar) and PbBr<sub>2</sub> (99.999%, Alfa Aesar) in a solvent consisting mixture of N,N-Dimethylformamide (DMF, anhydrous, 99.8%, Sigma Aldrich) and dimethyl sulfoxide (DMSO, GC,  $\geq$ 99.5%, Sigma Aldrich) (1.25 M with respect to Pb, DMF: DMSO=4:1). Perovskite layers were deposited onto the TMAH-FTO by spin coating the precursor using the anti-solvent process. The perovskite thin films were subsequently annealed at 100  $^{\circ}$ C for 60 min. For FTO/perovskite samples, FTO substrates should be treated with  $O_2$ -plasma for at least 20 min before perovskite deposition or visible pin-hole in perovskite layer appeared. For TMAH-FTO/perovskite, O<sub>2</sub>-plasma treatment process was skipped. The spiro-OMeTAD solution with bis(trifluoromethane) sulfonimide lithium salt (LTFSI, 99.95%, Sigma Aldrich) and 4-TBP (96%, Sigma Aldrich) was then grown onto the perovskite layer at 4000 rpm for 30 s. Finally, a 100 nm-thick gold top electrode was deposited by thermal evaporation. The active area of the device is  $0.09 \text{ cm}^2$ .

The conductivity of the thin films was studied using a conductive atomic force microscope (c-AFM, Bruker) in TUNA mode. Fourier Transform Infrared (FTIR) Spectra were collected by Nicolet 6700 (Thermo Scientific) from 400cm<sup>-1</sup> to 5000cm<sup>-1</sup>. X-ray-photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) were carried out on a Thermo Scientific ESCALab 250Xi, with the HeI (21.22 eV) emission line employed for excitation. The work function  $\Phi$  of the samples can be calculated by:  $\Phi$ =hv-(E<sub>cutoff</sub>-E<sub>Fermi</sub>), where hv= 21.22 eV and E<sub>Fermi</sub>=0 eV (using Ni as the standard sample for calibration). The steady state and time-resolved photoluminescence spectra of the perovskite

films were measured using a 1/4 m monochromator (Cornerstone<sup>TM</sup> 260) equipped with a silicon charge-coupled device (CCD) camera. The J-V measurement was carried out in ambient air using a Keithley-2400 source meter under simulated AM 1.5 G illumination (100 mW/cm<sup>2</sup>, Oriel Sol1A Class ABB Solar Simulator). The light intensity was calibrated with a silicon reference cell (NREL) equipped with a power meter. Reverse scan (1.2 V to -0.20 V, 0.01 V per step) was adopted for capturing the J-V curves of our PSCs. In order to study the hysteresis behavior, J-V curves were also obtained through forward scan (-0.2 V to 1.2 V, 0.01 V per step). The photo-electron conversion efficiency (IPCE) measurement was conducted using an Enli Tech (Taiwan) EQE measurement system. Mott-Schottky measurement and impedance spectroscopy was tested by CHI600A electrochemical workstation.



Fig. S1. Schematic diagram of C-AFM measurements conducted on FTO-TMAH and FTO-TMAH/perovkite.



Fig. S2. XPS survey scan for FTO and FTO-TMAH.



**Fig. S3.** XPS spectra of a) Sn3d, b) O1s and c) N1s for FTO and FTO-TMAH thoroughly rinsed for at least 3 times by water. A clear shift is observed in Sn3d and O1s binding energy after the TMAH treatment of FTO, indicating the strong interaction between FTO and TMAH. The emergence of N1s peak indicates the present of TMAH.



**Fig. S4.** FTIR spectra for TMAH on KBr quash slide (blue line), on FTO (red line) and on FTO after washed 3 times by water (wine line). The emergence of peaks located at 1731 cm<sup>-1</sup> indicates the O-N interaction between FTO and TMA<sup>+</sup>, even though the FTO-TMAH substrate was thoroughly rinsed for at least 3 times by water.



Fig. S5. Cut-off energy edge for bare FTO and FTO-TMAH surface. The inset is the UPS spectra.



**Fig. S6.** SEM images for perovskite layer on a) FTO and on b) FTO-TMAH substrate. AFM images for perovskite layer on c) FTO and d) FTO-TMAH substrate.



Fig. S7. UV-Vis and PL spectra of perovskite thin films on a) bare FTO and on b) FTO-TMAH.



**Fig. S8.** XPS survey scan for a) FTO/perovskite and b) FTO-TMAH/perovskite. c) The zoom-in XPS spectra showing the O1s, N1s and C1s peaks of FTO/perovskite and FTO-TMAH/perovskite. d) The N1s spectra of FTO/perovskite and FTO-TMAH/perovskite. The significant augment in N 1s, O 1s and C 1s peak intensity and element concentration for FTO-TMAH/perovskite and the binding energy peaks centered at 403.6 and 402.1 eV, which can be assigned to N 1s from TMA<sup>+</sup> and perovskite, respectively, indicate the presence of TMAH in the perovskite film.

Electrodes	С	Ν	Ο	Pb	Br	Ι
FTO/perovskite	9.0	6.75	2.5	27.3	34.5	22.2
FTO-TMAH/Perovskite	29.7	17.6	4.5	13.2	20.7	14.3

Table S1. Atom ratio (%) of elements in perovskite layer, obtained from the XPS results.



**Fig. S9.** The a) Pb 4f, b) I 3d and c) Br 3d spectra of FTO/perovskite and FTO-TMAH/perovskite. The absence of  $Pb^0$  in FTO-TMAH/perovskite indicates that the emergency of TMAH in perovskite film can effectively suppresses the formation of metallic Pb. The metallic element is commonly acts as centers for non-irradiative recombination



**Fig. S10.** The *J-V* curves of the PSCs constructed on FTO substrate modified by TMAH with various concentration (weight ratio), suggesting that the devices with 0.25 wt% TMAH-solution treatment give the best performance.

 Table S2. Photovoltaic parameters of PSCs constructed on FTO substrate modified by TMAH

 with various concentration (weight ratio).

Device	V <sub>oc</sub> (V)	$J_{\rm sc}$ (mA/cm <sup>2</sup> )	FF (%)	Efficiency (%)	$R_{ m sh} \ (\Omega \cdot  m cm^2)$	$R_{\rm s}$ ( $\Omega \cdot { m cm}^2$ )
0%	1.02	22.3	62.4	14.4	4635	87
0.1%	1.11	22.2	70.5	17.4	14649	73
0.25%	1.17	23.1	73.8	20.1	23299	93
0.5%	1.05	22.8	73.9	17.7	13499	69
1%	0.97	21.95	58.8	12.39	3200	81



Fig.S11. J-V characteristics for FTO based and FTO-TMAH based PSCs.



Fig. S12. a) The  $J_{sc}$  and b)  $V_{oc}$  of PSCs based on FTO and FTO-TMAH substrate as a function of light intensity. The  $J_{sc}$  is linear dependence of light density, indicating charge collection efficiency is rather independent of light intensity.



**Fig. S13.** *J-V* curves of forward scan (dot line) and reverse scan (solid line) for a) FTO based device and b) for FTO-TMAH-based device.

Device		$V_{ m oc}$	$J_{sc}$	FF	Efficiency
Denie		(V)	$(mA cm^{-2})$	ГГ	(%)
FTO-TMAH based	Reverse	1.17	23.22	0.739	20.1
	Forward	1.14	22.80	0.715	18.5
FTO based	Reverse	1.02	22.49	0.624	14.4
	Forward	0.93	21.97	0.315	6.5

Table S3. Photovoltaic properties of PSCs fabricated on bare FTO and on FTO-TMAH.



Fig. S14. Statistics of  $V_{oc}$ ,  $J_{sc}$ , FF and efficiency for 20 individual FTO-TMAH based devices.



Fig. S15. Stability test of bare FTO and FTO/TMAH based PSCs stored in the dark with a

humidity of 25±5% and a controlled temperature of 30°C.