Supporting Information

Developing gradient titanium dioxide/amorphous tantalum nitride electron transporting layer for efficient and stable perovskite solar cells

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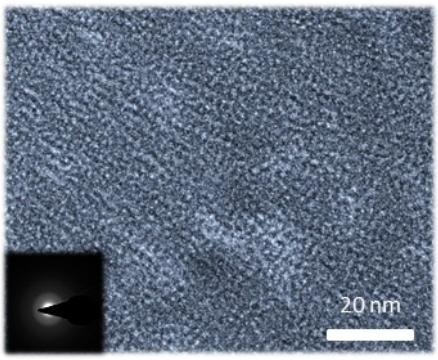

Fig. S1 TEM image of room-temperature deposited a-TaN_x film.

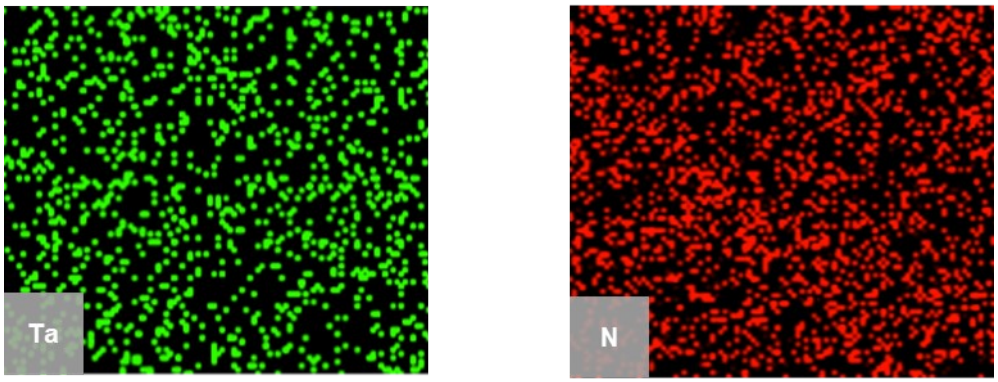

Fig. S2 EDS mapping of Ta and N elements.

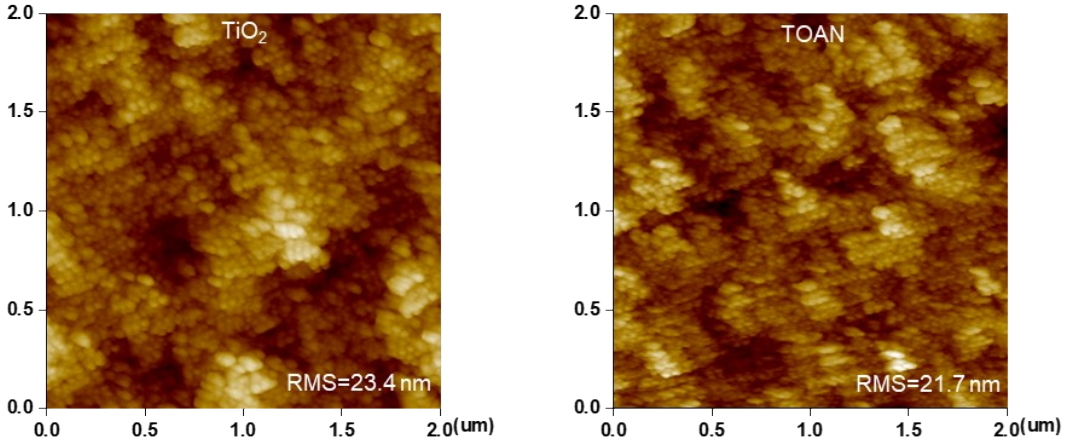

Fig. S3 Top-view AFM images of TiO_2 and TOAN films.

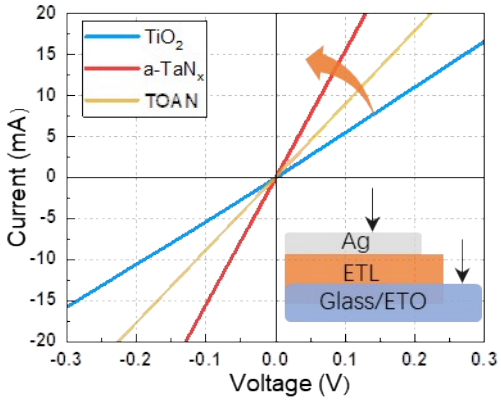

Fig. S4 *I–V* characteristics of TiO_2, TOAN and a-TaN_x films. Inset: Depiction of measurement architecture.

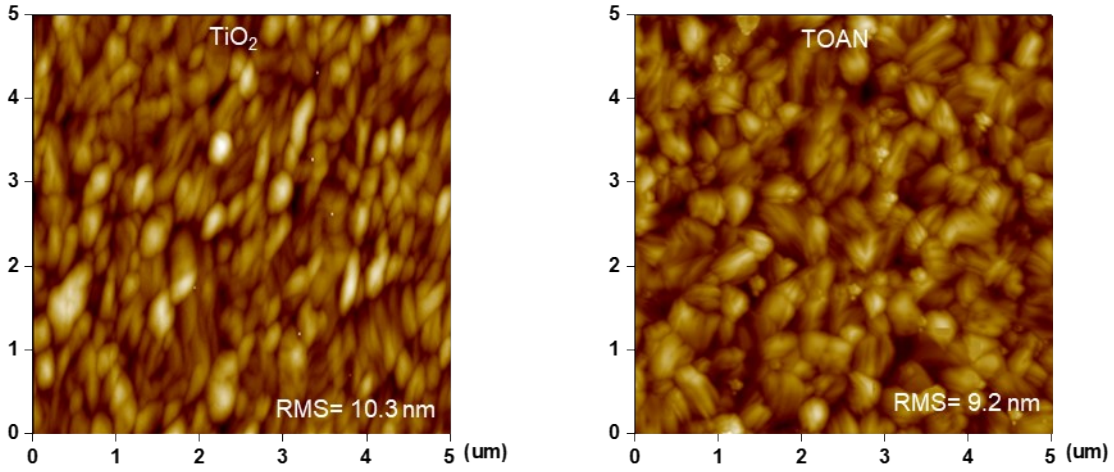

Fig. S5 AFM images of TiO_2- and TOAN- perovskite films.

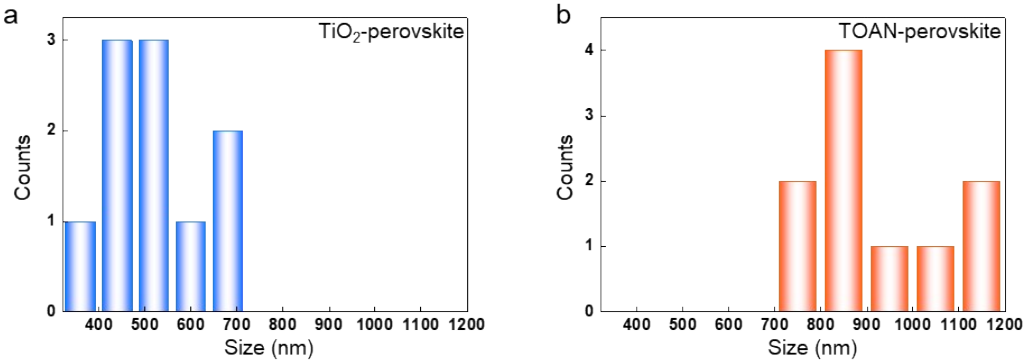

Fig. S6 The grain size distribution of TiO_2-perovskite and TOAN-perovskite, respectively.

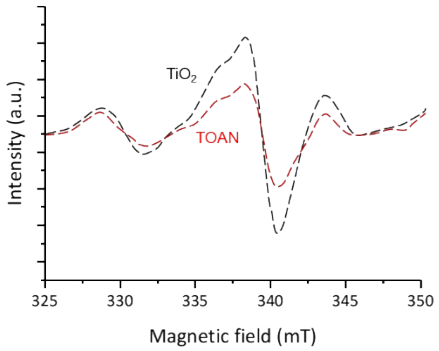

Fig. S7 EPR spectra of the TiO_2 and TOAN films.

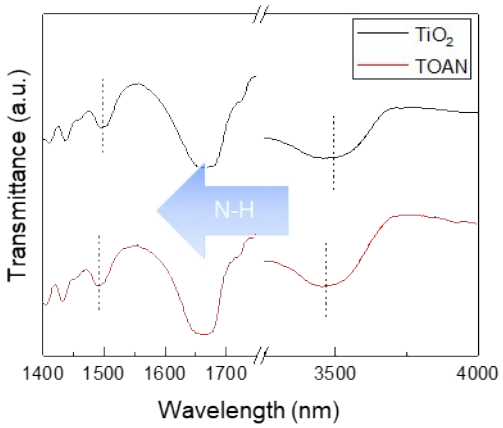

Fig. S8 FTIR spectra of the TiO_2- and the TOAN- perovskite from 1400 to 4000 cm^{-1}.

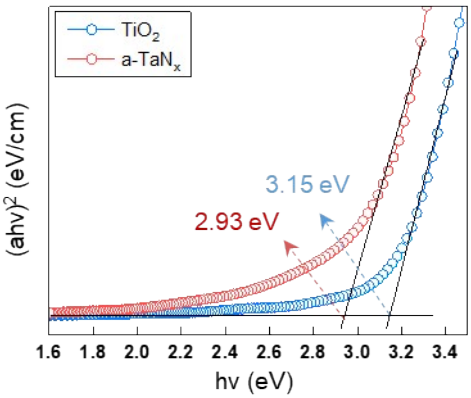

Fig. S9 The $(\alpha hv)^2$ versus hv plot for the TiO_2 and a-TaN_x, respectively.

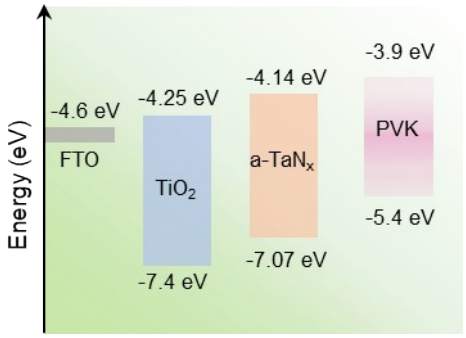

Fig. S10 Energy level diagram of perovskite films with different ETLs [1].

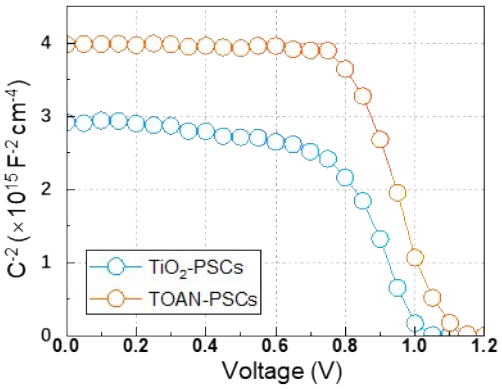

Fig. S11 Mott–Schottky analysis at 10k Hz of devices based on TiO_2 and TOAN ETL, respectively.

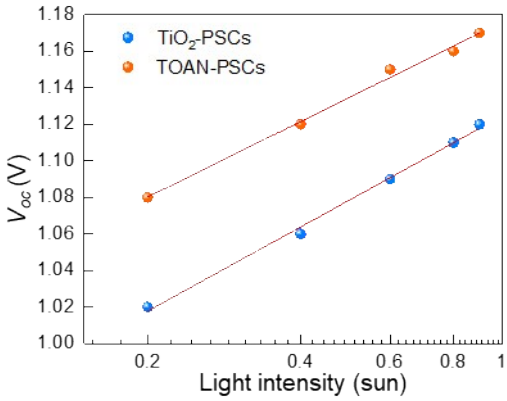

Fig. S12 V_{oc} of TiO_2- and TOAN- PSCs as a function of illumination intensity.

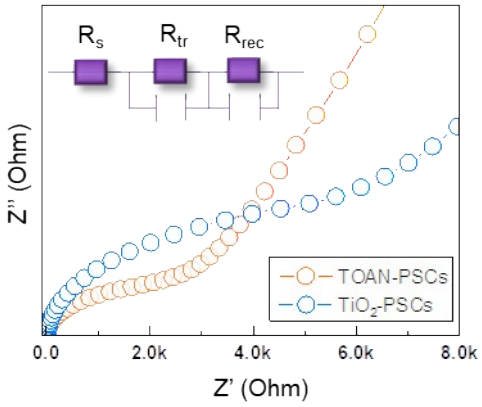

Fig. S13 EIS of perovskite devices based on the TiO_2 substrate and TOAN substrate. Inset: The equivalent circuit.

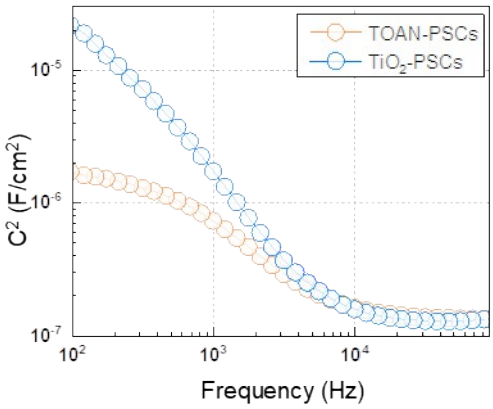

Fig. S14 Capacitance-frequency curves of the PSCs based on TiO_2 and TOAN ETLs.

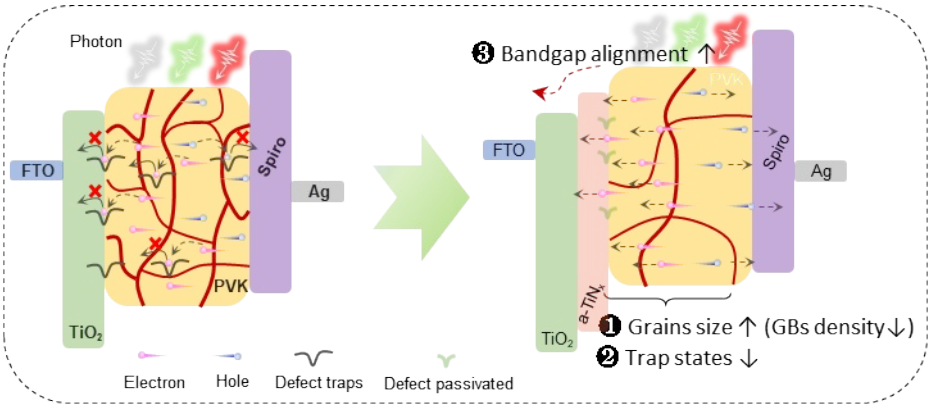

Fig. S15 Schematic illustration of charge traps and transport for TiO_2- and TOAN-device.

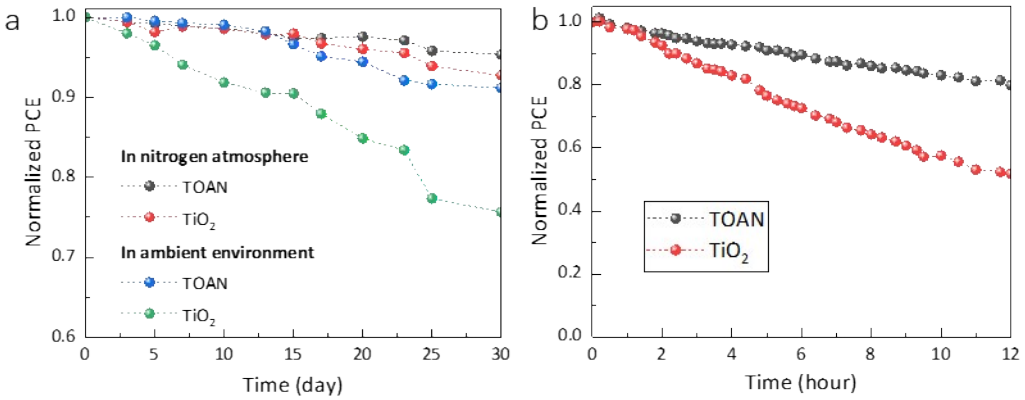

Fig. S16 (a) The normalized *PCE* of the TiO_2- and TOAN- devices in nitrogen atmosphere and ambient environment. (b) The operational stability of the TiO_2- and TOAN- devices.

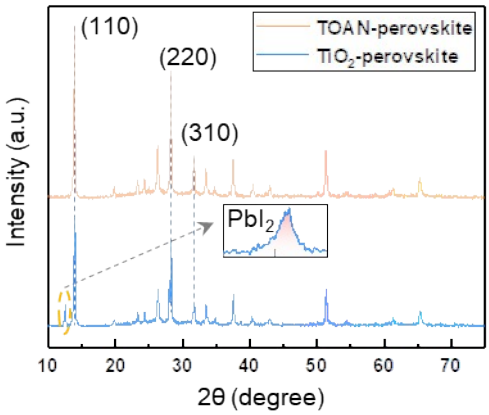

Fig. S17 XRD patterns of the bare perovskite films grown on TiO_2 or TOAN ETLs, respectively. These films are stored for 3 days in ambient with ~42% humidity.

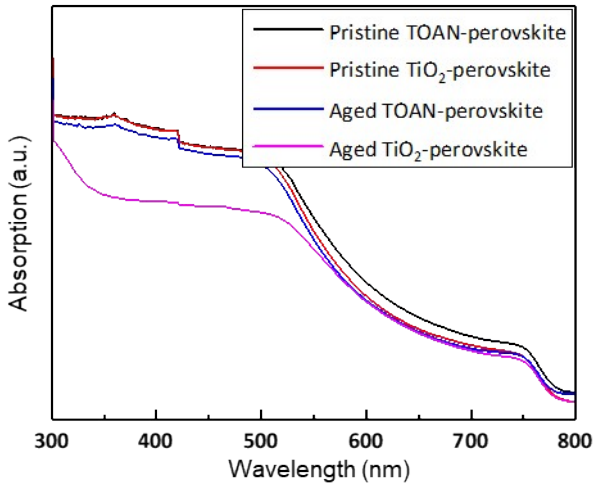

Fig. S18 UV-vis absorption spectra of TiO_2-perovskite and TOAN-perovskite films in an atmospheric environment with a temperature of 25°C and a humidity of ~42%.

Table S1. TRPL lifetimes of TiO_2-perovskite and TOAN-perovskite, respectively.

Sample	y_0	A_1	t_1 (ns)	A_2	t_2 (ns)
TiO_2	0.0059	0.7457	14.57	0.1844	79.9
TOAN	0.0026	0. 5805	3.92	0.415	23.29

Table S2. Detail values of V_{oc}, J_{sc}, *FF* and *PCE* for TOAN and TiO_2 devices.

Sample	V_{oc} (V)	J_{sc} (mA cm^{-2})	*FF* (%)	*PCE* (%)
TOAN cell-R	1.20	22.87	78.03	21.41
TOAN cell-F	1.20	22.65	78.47	21.32
TiO_2 cell-R	1.14	21.75	76.74	19.02
TiO_2 cell-F	1.14	20.38	74.68	17.35

Table S3. The output parameters of the TiO_2-based devices.

	V_{oc} (V)	J_{sc} (mA cm^{-2})	*FF* (%)	*PCE (%)*
1	1.16	21.61	74.38	18.64
2	1.16	20.38	74.38	17.58
3	1.16	20.76	73.93	17.80
4	1.17	21.15	64.69	16.00
5	1.16	21.30	64.69	15.98
6	1.14	22.89	65.72	17.14
7	1.15	22.39	52.45	13.50
8	1.16	22.73	48.73	12.84
9	1.15	23.10	66.29	17.60
10	1.13	19.92	63.75	14.34
11	1.08	19.55	70.86	14.96
12	1.04	18.50	71.43	13.74
13	1.13	20.91	67.89	16.04
14	1.18	22.39	71.65	18.93
15	1.13	21.68	70.24	17.20
16	1.04	17.42	78.96	14.30
17	1.13	21.49	74.96	18.20
18	1.16	21.38	67.09	16.63
19	1.17	22.31	73.02	19.06
20	1.17	21.43	75.53	18.93

Table S4. The output parameters of the TOAN-based devices.

	V_{oc} (V)	J_{sc} (mA cm^{-2})	*FF* (%)	*PCE (%)*
1	1.19	22.00	76.95	20.14
2	1.19	22.16	77.85	20.52
3	1.19	21.07	77.25	19.36
4	1.17	22.22	78.27	20.34
5	1.16	22.84	76.75	20.33
6	1.19	22.11	77.85	20.48
7	1.19	22.85	77.73	21.13
8	1.17	22.07	76.20	19.67
9	1.15	20.60	76.47	18.11
10	1.14	21.04	73.31	17.58
11	1.19	20.38	74.84	18.15
12	1.17	20.21	76.40	18.06
13	1.19	22.71	77.85	21.03
14	1.16	22.75	77.35	20.41
15	1.19	21.83	74.61	19.38
16	1.13	22.60	76.35	19.49
17	1.15	22.70	77.13	20.13
18	1.14	22.53	76.78	19.72
19	1.18	20.61	77.56	18.86
20	1.16	20.60	75.59	18.06

Supplementary Note 1

Preparation of TOAN ETL: FTO needs to be washed four times with deionized water and alcohol, respectively. Each time requires ultrasonic treatment 20 minutes. The s-TiO_2 is prepared with isopropanol and n-butanol in the ratio of 1:10.3, covering the surface of the FTO with a spin coating method at 2000 revolutions per minute (RPM) for 30 s and then annealed at 135 °C for 10 min. In order to prepare m-TiO_2, colloidal TiO_2 (Dyesol 18NRT) is required to be dissolved in alcohol at a ratio of 1:7 then the m-TiO_2 is spin-coated on the s-TiO_2 at a speed of 4000 rpm for 30 s and the same annealing is done for 10 min at 135 °C. After the above steps, the samples are calcined in a muffle furnace at 500 ℃ for 30 min. The a-TaN_x layer was deposited using a sputtering technique. The target used was a tantalum nitride (Ta:N=1:2). The sputtering deposition was carried out under a vacuum degree of 5×10^{-4} Pa. The sputtering power and time were 100 W and 15 min, respectively.

Solar Cell Fabrication: 462 mg of PbI_2 and 163 mg of MAI were dissolved in a mixed solvent of Dimethyl sulfoxide (DMSO) and Dimethylformamide (DMF) (v: v = 3:7) and stirred at 70 ^oC. The 90 μL of the mixture was deposited on the FTO/TOAN layer by a two-step continuous spin coating process, i.e., 500 RPM for 10 s and 4500 RPM for 30 s to form $MAPbI_3$ films. During the second step, 400 μL of CB was poured on the spinning substrate 15 s prior to the end of the program. Subsequently, the obtained films were dried at 60 ^oC for 5 min and at 100 ^oC for 10 min. Then, hole transport layers were prepared by mixing 72.3 mg of Spiro-OMeTAD, 18.5 μL with a solution of 500 mg/mL Li-TFSI in acetonitrile and 28.5 μL of 4-tert-butylpyridine in 1

mL of chlorobenzene. The 75 μL of the mixture solution was spin-coated on the prepared $MAPbI_3$ films at 3000 RPM for 30 s. Finally, 100 nm Ag was thermally deposited under vacuum condition.

Supplementary Note 2

Materials: Fluorine-doped tin oxide (FTO) 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). Titanium diisopropoxide bis (acetylacetonate) were purchased from Sigma-Aldrich. All chemicals and reagents were used as received from chemical companies without any further purification.

Supplementary Note 3

Characterization: The scanning electron microscope (SEM) images were taken using Hitachi S-4800 and Zeiss sigma 500. 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. The atomic force microscopy (AFM) images were taken by Park NX20. X-ray photoelectron spectroscopy (XPS) was performed by using Escalab250Xi. The Fourier transform infrared (FTIR) spectra was taken by using Nicolet iS50. *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. PL spectra were obtained using a PL microscopic spectrometer (FLS1000, England) with a 405 nm CW laser excitation source. The TRPL (FLS1000, England) 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.

Reference

[1] F. Wang, M. Yang, Y. Zhang, J. Du, D. Han, L. Yang, L. Fan, Y. Sui, Y. Sun, X. Meng, J. Yang, Constructing m-TiO_2/a-WO_x hybrid electron transport layer to boost interfacial charge transfer for efficient perovskite solar cells, Chem. Eng. J. 402 (2020) 126303