Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Supporting Information

High Efficiency Flexible Perovskite Solar Cells using Superior Low Temperature TiO_2

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Experimental section

Synthesis of CH_3NH_3I:

Methylamine (12 mL, 33 wt.% in absolute ethanol, Aldrich) and hydroiodic acid (5 mL, 57 wt.% in water, Aldrich) were mixed in 100 mL round-bottom flask at 0 ℃ for 2 h with stirring. The precipitate was recovered by removing the solvents at 50 ℃ using a rotary evaporator. Re-dissolve the product in absolute ethanol, precipitate by adding certain amount of diethyl ether. After filtration, the above steps were repeated for one more time to harvest pure CH_3NH_3I material. Finally, the solid product was dried at 60 ℃ in a vacuum oven for 24 h.

Preparation of the TiO_2 layer

Glass/ FTO, glass/ITO and PET/ITO were cleaned with acetone, isopropyl alcohol and deionized water successively in ultrasonic baths for 30 min, and then dried by flowing nitrogen gas. The TiO_2 films were sputtered on various substrates by the PVD-75 vacuum system (Kurt J. Lesker, U.S.A). DC magnetron sputtering power was 200 W using a 3-inch-diameter metallic plate of Ti (99.995%) in an atmosphere of Ar (99.998%) and O_2 (99.998%). The Ar/O_2 gas flow ratio was kept at 100:15 during deposition by mass-flow-controlled gas inlets. The base pressure of the system was less than 1.5×10^{-7} Torr. The sputtering pressure was kept at 7.5×10^{-3} Torr with a mixture gas of Ar and O_2 during the sputtering processes. Before deposition, the target was pre-sputtered for 5 min in order to remove the oxide layer on the target surface. The thickness of the 60-70 nm TiO_2 film was determined by a Bruker 150 surface profiler. For comparison, some TiO_2 thin film samples were annealed at 500 ℃ for 30 min before deposition of perovskite films.

Fabrication of the perovskite solar cells

For the perovskite solar cell fabrication, the perovskite films were deposited on 33 mm × 33 mm substrate by a thermal evaporation system with ceramic crucible boat for $PbCl_2$. (1) 150 nm thick $PbCl_2$

film was deposited onto the substrate by evaporation at 310 ℃. The deposition rate was maintained at ca. 1 Å s^{-1} and substrate at room temperature. (2) Upon cooling for about 1 hour, the $PbCl_2$ coating was transferred into the nitrogen filled glovebox. (3) Uniformly distribute a layer of CH_3NH_3I powder onto a 70 mm × 70 mm aluminum plate (Fig. S9). (4) Place the $PbCl_2$ coating on the CH_3NH_3I layer, heat them to 150 ℃ and maintain at the temperature for 20 min to ensure all $PbCl_2$ transformed into perovskite. (5) Transfer the perovskite sample into a petri dish and cooled it for 30 min. (6) Wash the perovskite with 50 mL isopropanol, dry it in flowing nitrogen, and then annealed it at 70 ℃ for 5 min. For the HTL, 90 mg spiro-OMeTAD, 36 μL 4-tert-butylpyr-idine, and 22 μL of a solution of 520 mg/mL lithium bis(trifluoromethylsulphonyl) imide in acetonitrile were dissolved in 1mL chlorobenzene, the solution was then spin-coated onto the perovskite film at 4500 rpm for 1 min. The thickness of the spiro-OMeTAD film was determined by a Bruker 150 surface profiler to be ~170 nm. Finally, Au electrode was deposited by a thermal evaporator to a thickness of 80 nm.

Characterization

The J-V curves were measured using a computer-controlled Keithley 2400 source measure unit under ambient conditions, and the illumination intensity was 100 mW cm^{-2} (AM 1.5G Oriel solar simulator, calibrated by a NREL-traceable KG5 filtered silicon reference cell). An aperture area of 1.134 mm^2 was used during the measurement to define the active area of the device and to avoid light scattering through the sides. All devices scanned from negative bias to positive bias with standard test procedure at scan rate 0.2 V s^{-1}. The IPCE was characterized on the QTest Station 2000ADI system (Crowntech. Inc., USA), and a light source is xenon lamp for 300 W. The monochromatic light intensity for IPCE was calibrated using a reference silicon photodiode.

The KPFM measurements were carried out on the non-contact AFM (Bruker Metrology Nanoscope VIII AFM) in ambient atmosphere. The topography of the samples was tested by means of the change of the cantilever’s resonance frequency. Typical scan line frequency was 0.5 Hz and each image contained 512 × 512 pixels. The scan size for all images is controlled to 1x1 μm^2. Using a tip with a known Fermi level (-4.60 eV) of the highly oriented pyrolytic graphite as reference sample allows to derive the sample’s Fermi level.

The steady state PL spectra were obtained with Edinburgh Instruments FLS920 fluorescence spectrometer. TRPL spectra were acquired using the time-correlated single photon counting method with an Edinburgh Instruments FLS920 fluorescence spectrometer. The excitation source is a picosecond pulsed diode laser at 406.8 nm with the pulse width 64.2 ps. All decays were measured using a 4096-channel analyzer in ambient condition.

Using FTO substrates, the TiO_2 films were prepared with and without annealing for 30 min at different temperatures. GI-WAXS experiment was performed. For the best sensitivity, the 10 keV X-ray beam was incident at a grazing angle of 1° from the sample.

The HRTEM image and electron diffraction pattern were taken using JEM-2100 microscopy operated at 200 eV. The SEM images were taken using a Quanta 200F microscope (FEI Company) with an accelerating voltage of 0.5 - 30 kV. The light transmission spectra were acquired using a Varian UV–Vis spectrometer, Cary 5000.

References

1. D. Yang, P. Fu, F. Zhang, N. Wang, J. Zhang and C. Li, *J. Mater. Chem. A*, 2014, **2**, 17281.

2. A. Hexemer, W. Bras, J. Glossinger, E. Schaible, E. Gann, R. Kirian, A. MacDowell, M. Church, B. Rude, H. Padmore, *J. Phys.: Conf. Ser.*, 2010, **247**, 012007.

3. S. Sadewasser, *phys. stat. sol. (a)*, 2006, **203**, 2571.

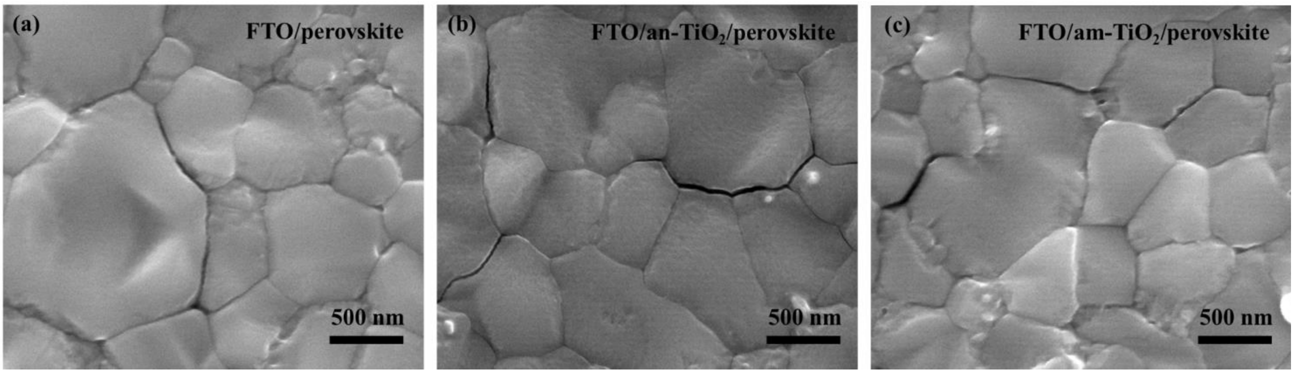

Fig. S1. SEM images of the perovskite films grown on (a) FTO, (b) an-TiO_2 and (c) am-TiO_2 substrates.

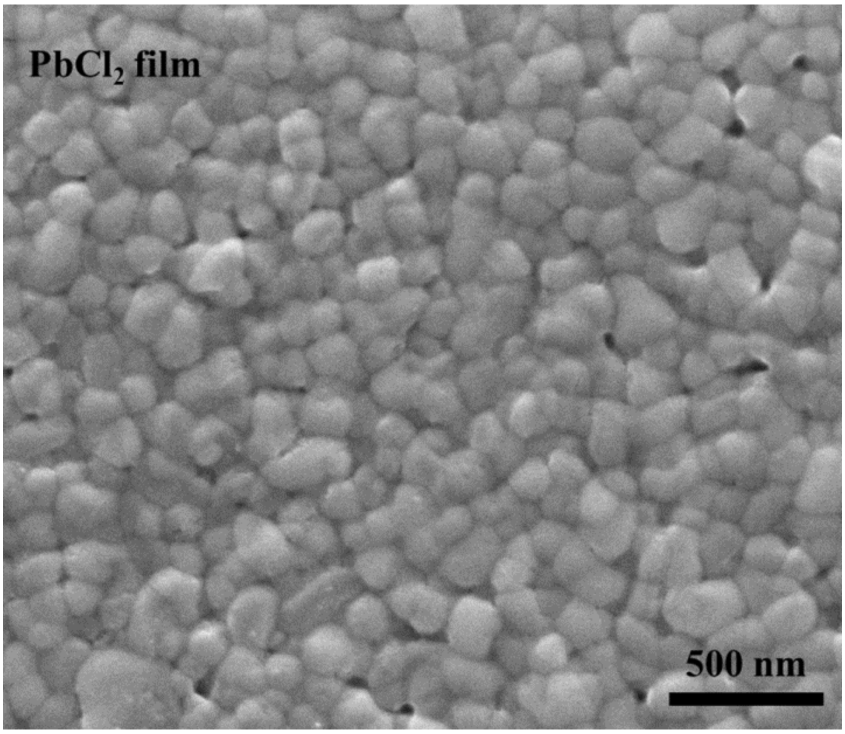

Fig. S2. SEM images of the $PbCl_2$ films.

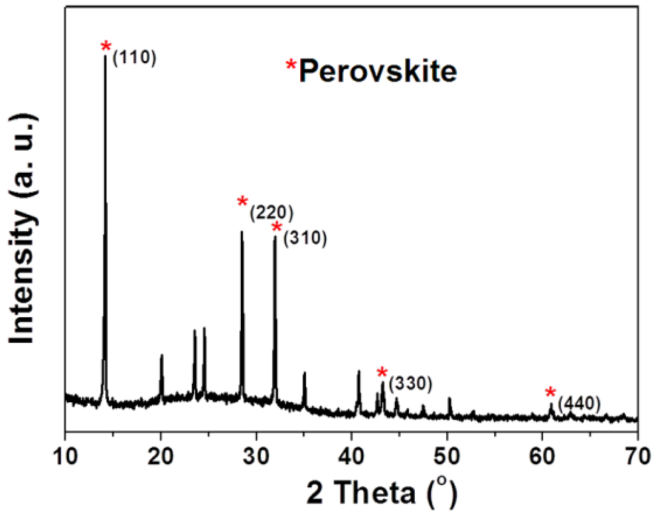

Fig. S3. XRD of perovskite film.

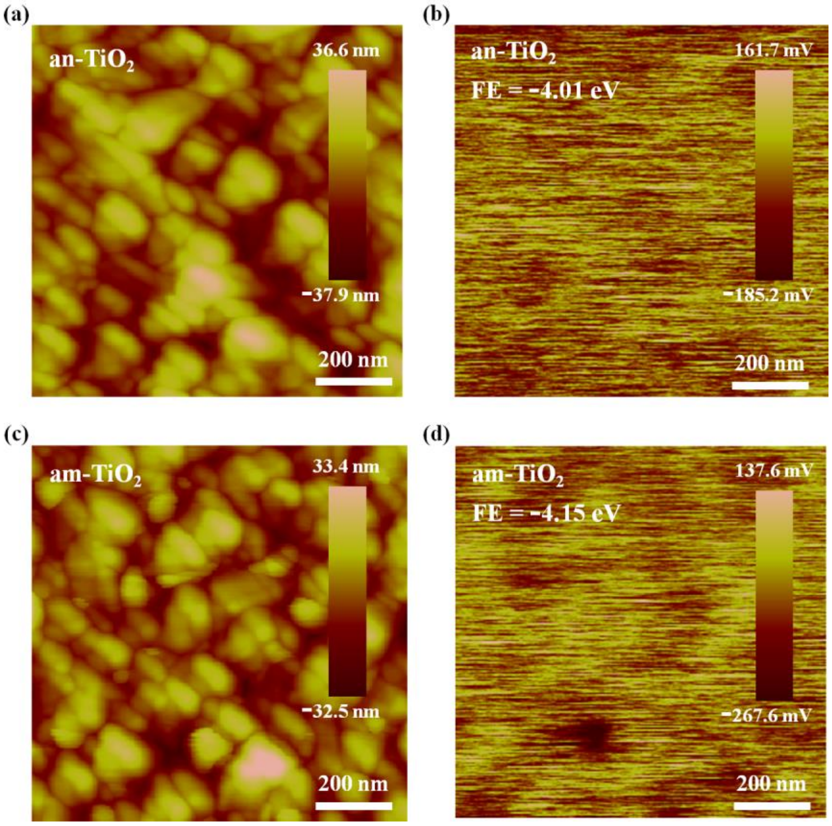

Fig. S4. The KPFM measurements of the TiO_2 thin films. The topography images of (a) the an-TiO_2 and (c) am-TiO_2. Surface potential images of (b) the an-TiO_2 and (d) am-TiO_2 films.

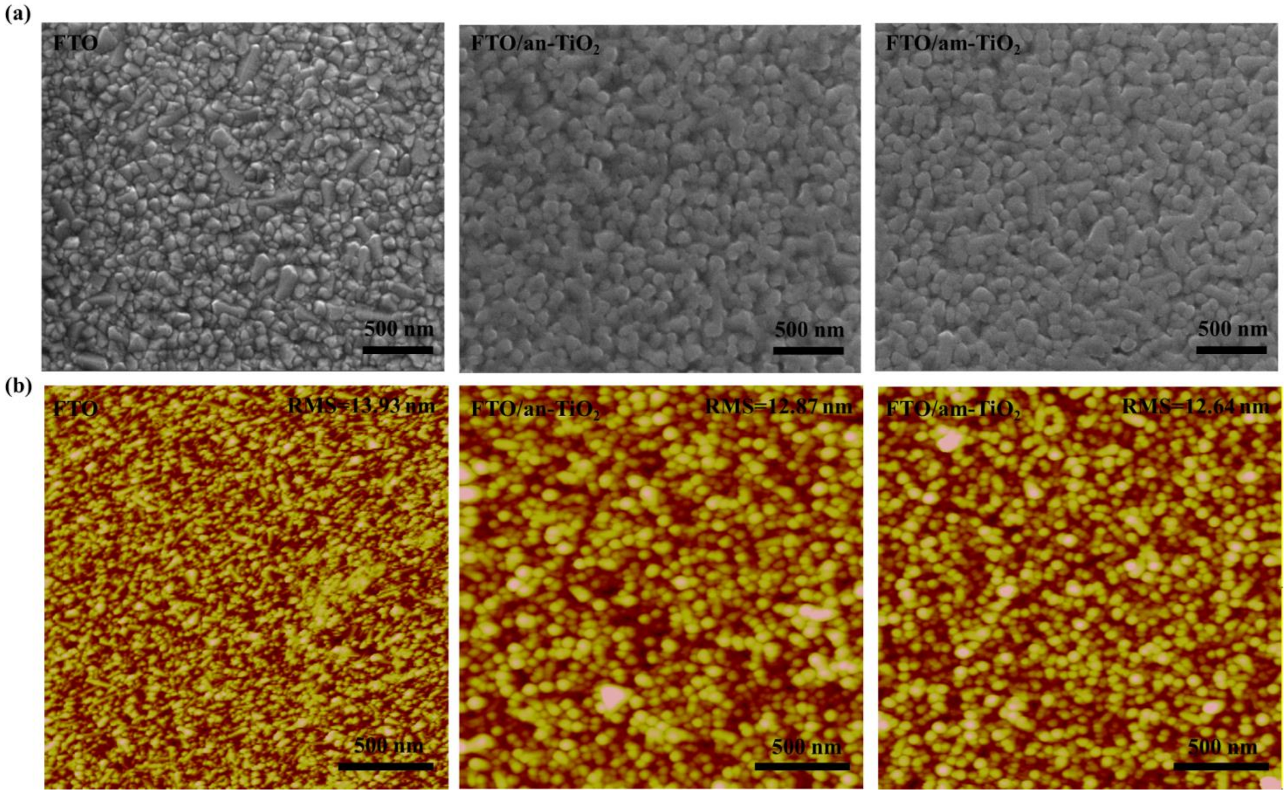

Fig. S5. (a) SEM images of FTO, an-TiO_2 film and am-TiO_2 films. (b) AFM images of FTO, an-TiO_2 and am-TiO_2 films.

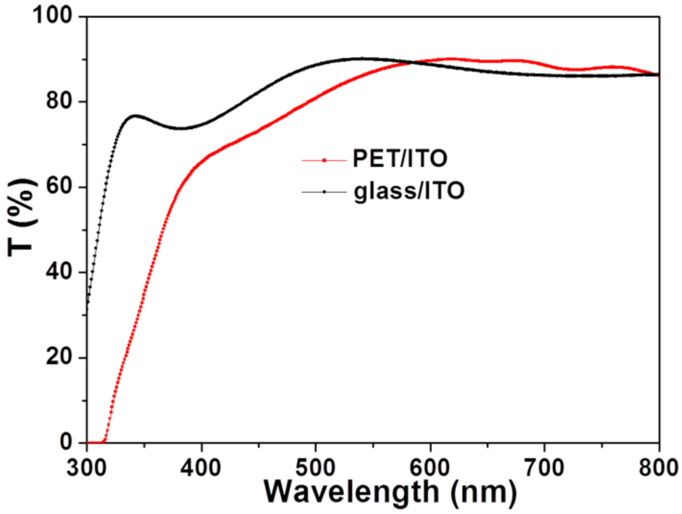

Fig. S6. Optical transmission spectra of glass/ITO and PET/ITO.

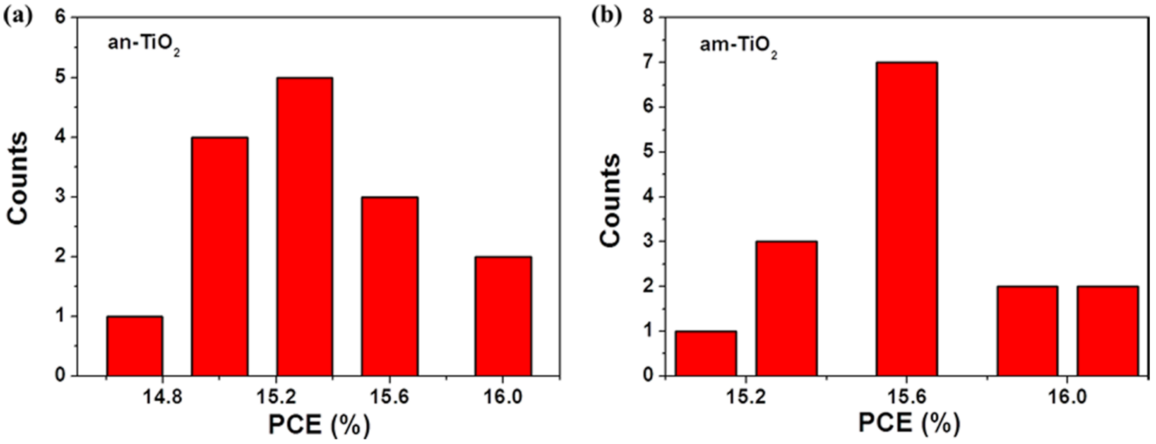

Fig. S7. The PCE histogram distribution diagrams of perovskite solar cells with (a) an-TiO_2 and (b) am-TiO_2 as ETLs.

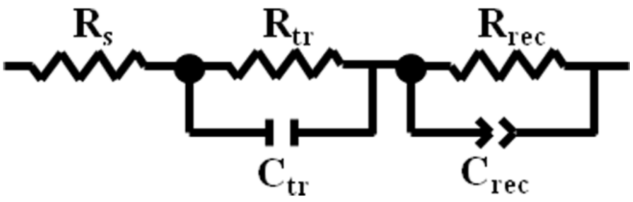

Fig. S8. The equivalent circuit model for perovskite solar cells in EIS.

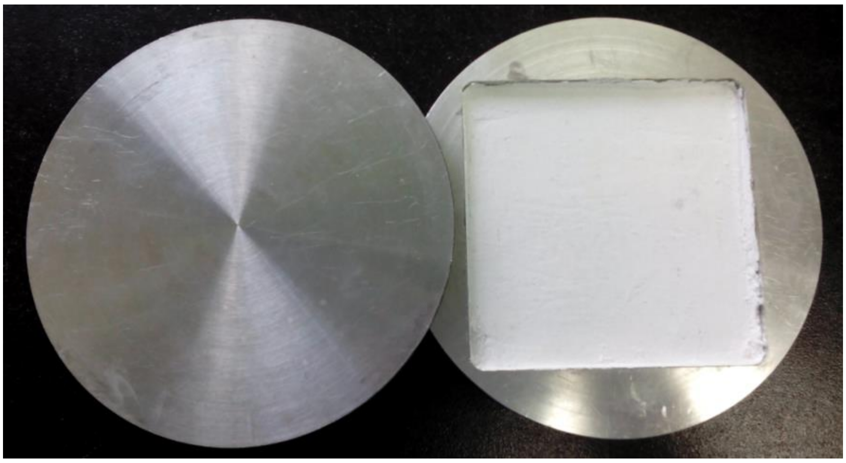

Fig. S9. The aluminum plate with a uniform layer of CH_3NH_3I powder.

Table S1. The parameters of flexible solar cells using am-TiO_2 ETLs and rigid solar cells using am-TiO_2 or an-TiO_2 ETLs.

Flexible cells	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	PCE (%)
1	20.22	1.02	0.69	14.23
2	20.06	1.02	0.69	14.12
3	20.38	1.00	0.70	14.27
4	20.42	0.98	0.69	13.81
5	19.90	1.02	0.67	13.60
6	20.45	0.98	0.66	13.23
7	19.50	1.00	0.70	13.65
8	21.11	1.00	0.69	14.57
9	21.12	1.02	0.68	14.65
10	20.66	0.98	0.66	13.36
11	20.90	1.03	0.70	15.07
12	20.27	1.00	0.68	13.78
13	20.30	1.00	0.70	14.21
14	20.31	1.02	0.70	14.50
15	20.11	1.03	0.69	14.29
Average	20.38 ± 0.43	1.01 ± 0.02	0.69 ± 0.01	14.09 ± 0.50

Rigid cells an-TiO_2	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	PCE (%)
1	19.93	1.08	0.69	14.85
2	20.67	1.07	0.67	14.82
3	20.71	1.08	0.68	15.21
4	19.74	1.08	0.69	14.71
5	21.61	1.08	0.67	15.64
6	21.43	1.08	0.68	15.74
7	21.64	1.06	0.68	15.60
8	22.21	1.06	0.66	15.54
9	21.08	1.08	0.67	15.26
10	20.05	1.07	0.69	14.81
11	21.31	1.08	0.69	15.88
12	21.14	1.08	0.68	15.52
13	19.43	1.08	0.72	15.11
14	20.90	1.09	0.68	15.49
15	21.61	1.08	0.69	16.10
Average	20.90 ± 0.80	1.08 ± 0.01	0.68 ± 0.01	15.35 ± 0.43

Rigid cells am-TiO_2	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	PCE (%)
1	20.97	1.03	0.72	15.55
2	21.63	1.02	0.71	15.66
3	22.12	1.02	0.71	16.02
4	21.39	1.02	0.72	15.71
5	21.57	1.03	0.70	15.55
6	21.53	1.03	0.70	15.53
7	21.76	1.03	0.69	15.46
8	21.20	1.00	0.72	15.27
9	22.18	1.02	0.71	16.06
10	21.57	1.00	0.72	15.53
11	21.69	1.01	0.70	15.33
12	21.42	1.02	0.71	15.52
13	21.28	1.01	0.71	15.26
14	21.87	1.01	0.72	15.91
15	21.87	1.03	0.72	16.22
Average	21.60 ± 0.32	1.02 ± 0.01	0.71 ± 0.01	15.64 ± 0.25

Table S2. Parameters of the time-resolved photoluminescence (TRPL) spectroscopy based on the glass/perovskite, an-TiO_2/ perovskite and am-TiO_2/ perovskite, respectively.

Samples	τ_{ave} (ns)	τ_1 (ns)	Amplitude of τ_1 (%)	τ_2 (ns)	Amplitude of τ_2 (%)	k_{et} (s^{-1})
Glass/perovskite	20.98	20.98	100	/	/	/
An-TiO_2/ perovskite	11.72	17.34	25.27	4.71	74.73	3.77×10^7
Am-TiO_2/ perovskite	4.68	12.68	4.68	1.66	95.32	1.66×10^8

Table S3. EIS parameters of the perovskite cells with and without the ETLs.

	w/o	an-TiO_2	am-TiO_2
R_s (Ω)	35.1	35.3	38.5
R_{tr} (Ω)	1337	779.1	504.1
R_{rec} (Ω)	5303	9724	6771
C_{tr} (F)	1.95×10^{-8}	2.51×10^{-8}	6.70×10^{-8}
C_{rec} (F)	8.46×10^{-8}	6.22×10^{-8}	7.21×10^{-8}