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

Supporting Information

ITIC Surface Modification to Achieve Synergistic Electron Transport Layer Enhancement for Planar-Type Perovskite Solar Cells with Efficiency Exceeding 20%

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UPS measurement:

UPS is usually used to determine the Fermi level (E_F) and the valence band maximum (E_V) with respect to vacuum level (E_{VAC}) of the fabricated thin films.[1,2] For a photoelectron to escape the sample surface and to be collected, it has to have sufficient energy to overcome the sum of the binding energy (with respect to E_F) of its initial level and the work function (Φ), where $\Phi = E_{VAC} - E_F$. Therefore, for a fixed incident photon energy of 21.22 eV, the secondary electron cut-off (high binding energy edge) represents photoelectrons with zero kinetic energy when they escape from the sample surface. The work function Φ is determined by the difference between the incident photon energy (21.22 eV) and the binding energy of the secondary electron cut-off. The difference between E_F and E_V is determined by the intersection of the linear portion of the spectra near the Fermi edge (low binding energy region) with the baseline. **Figure 4b** shows the UPS data which allows us to determine the work function of both TiO_2 and TiO_2 coated with ITIC.

TRPL measurement:

The TRPL decay time and amplitudes are obtained using an exponential Equation (1): [3,4]

$$f(x) = \sum_i A_i \exp(-t/\tau_i) + K \qquad (1)$$

where A_i is the decay amplitude, τ_i is the decay time and K is a constant for the base-line offset. To understand the recombination mechanism of the perovskite thin films on different substrates, the recombination kinetics was modelled over a range of excitation intensities using the following Equation (2): [3,4]

$$-\frac{dn}{dt} = An + Bn^2 + Cn^3 \qquad (2)$$

where n is the photogenerated excess carrier density and t is the time. The physical interpretations of these three terms are (i) the first-order decay rate is due to the trap-mediated (Shockley-Hall-Read) recombination at low injection condition; (ii) the second-order decay rate is due to the non-geminate/free carrier recombination at high injection; and (iii) the third order decay rate is for the Auger recombination. When TiO_2/perovskite or TiO_2/ITIC/perovskite is analyzed, the tremendous second-order decay rate is observed for the photogenerated carrier easy injection from perovskite to the TiO_2 ETL. Based on the above analysis, the PL decay time obtained by bi-exponential function is used to fit the PL decay time.

Reference:

[1]. C.-H. M. Chuang, P. R. Brown, V. Bulović & M. G. Bawendi. *Nat. Mater.* **2014**, *13*, 796-801.

[2]. Z. Jin, Q. Zhou, Y. Chen, P. Mao, H. Li, H. Liu, J. Wang & Y. Li. *Adv. Mater.* **2016**, *28*, 3697-3702.

[3]. J. S. Manser & P. V. Kamat. *Nat Photon* **2014**, *8*, 737-743.

[4]. B. S. Tosun & H. W. Hillhouse. *J. Phys. Chem. Lett.* **2015**, *6*, 2503-2508.

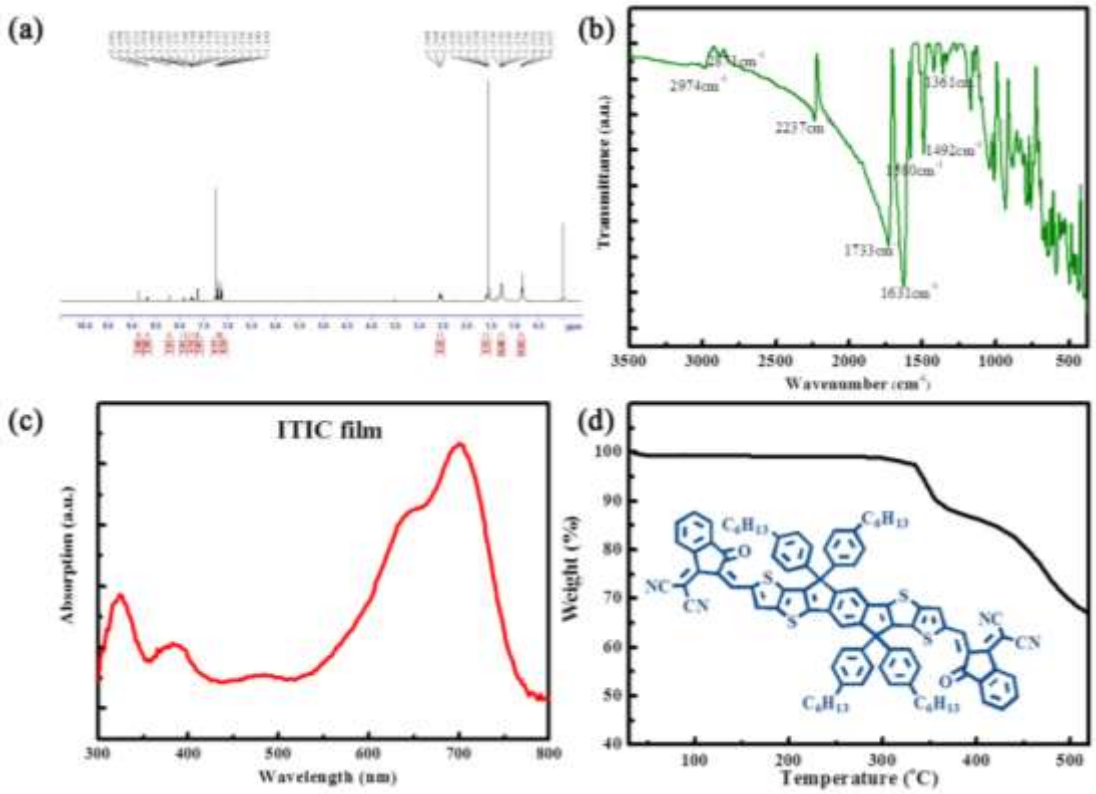

Figure S1. The properties of ITIC: (a) H-NMR, (b) FTIR spectrum, (c) film absorption spectrum and (d) TGA curve and the molecular structure.

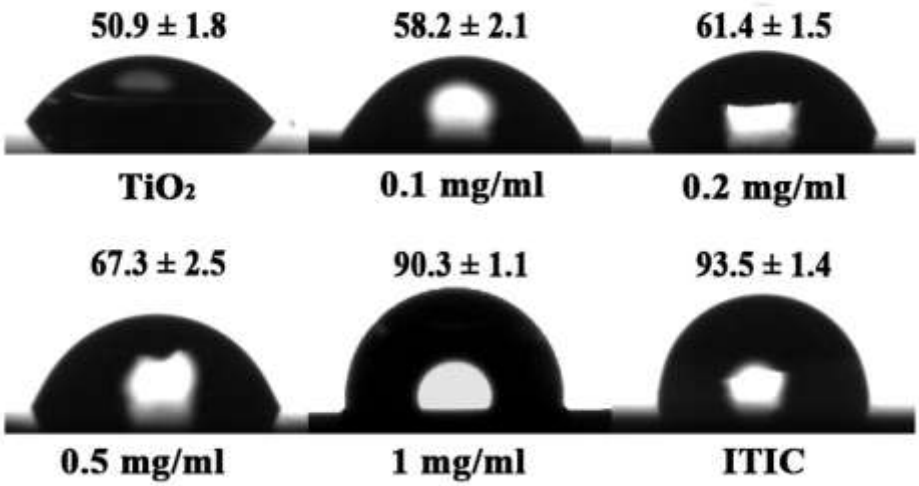

Figure S2. Photographs of water droplet on: pristine TiO_2 film, different concentrate ITIC modified TiO_2 film and pristine ITIC film.

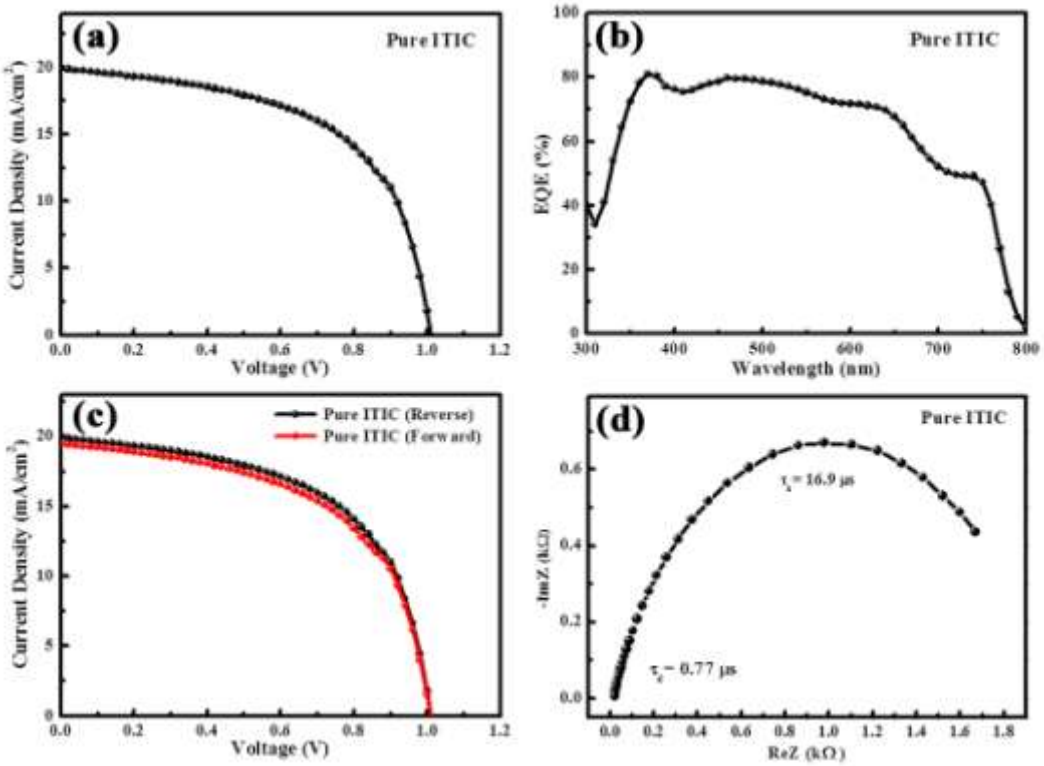

Figure S3. Properties of the perovskite solar cells based on ITIC ETL: (a) for J-V characteristics, (b) for EQE curve, (c) for J-V characteristics with different sweep directions (scan rate 200mV/s), (d) for IS result.

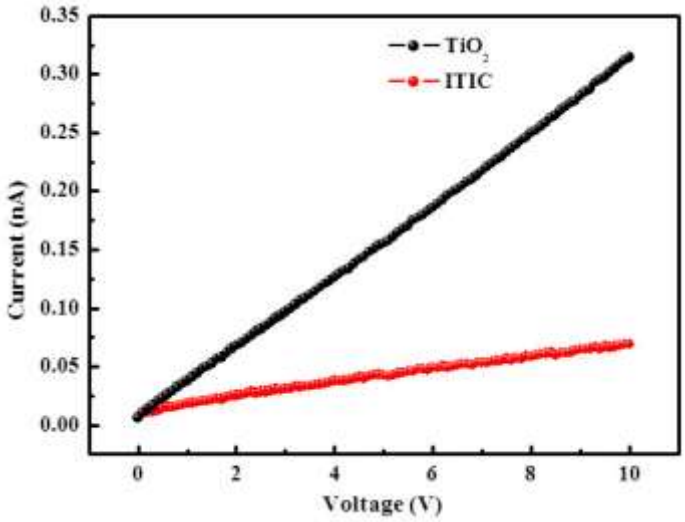

Figure S4. Conductivities of pristine TiO_2 film and pristine ITIC film.

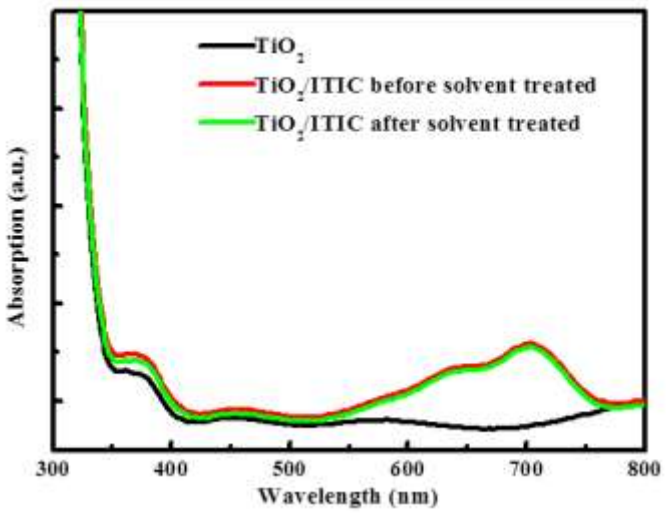

Figure S5. The UV-vis analysis of ITIC films before and after DMSO and GBL mixed solvent (3:7 v/v) treatment.

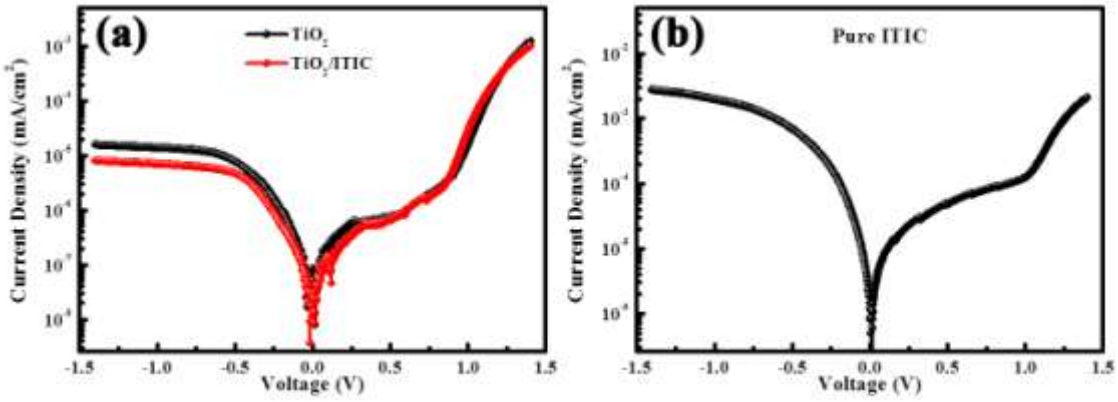

Figure S6. J-V characteristics of the fabricated perovskite photovoltaic solar cells with different ETL in dark condition: (a) for TiO_2 ETL and TiO_2/ITIC ETL, (b) for ITIC ETL.

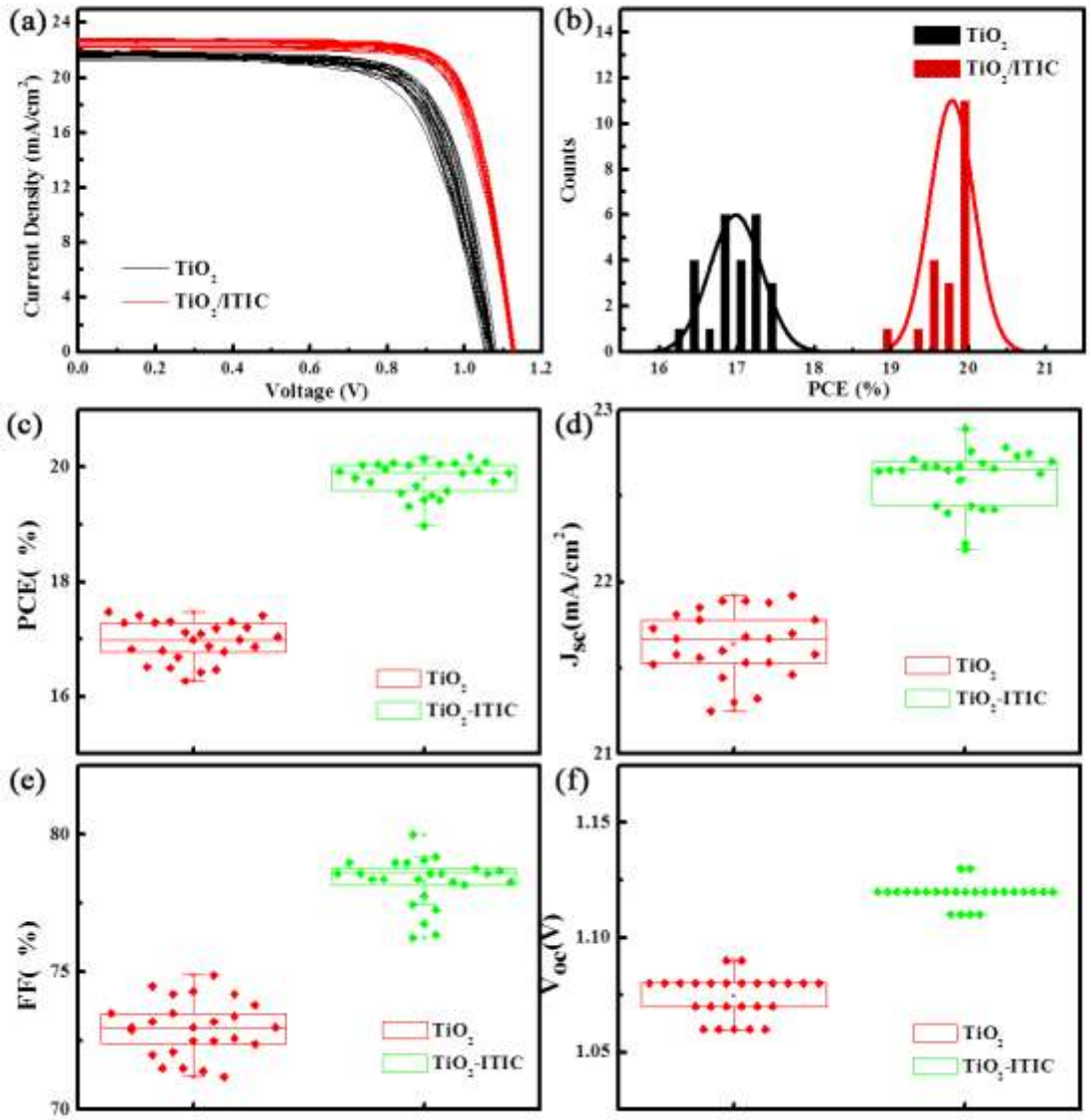

Figure S7. 25 individual devices were fabricated: (a) for J-V characteristics; (b) for the PCE distribution histograms; (c) for PCE distribution; (d) for J_{SC} distribution; (e) for FF distribution; and (f) for V_{OC} distribution.

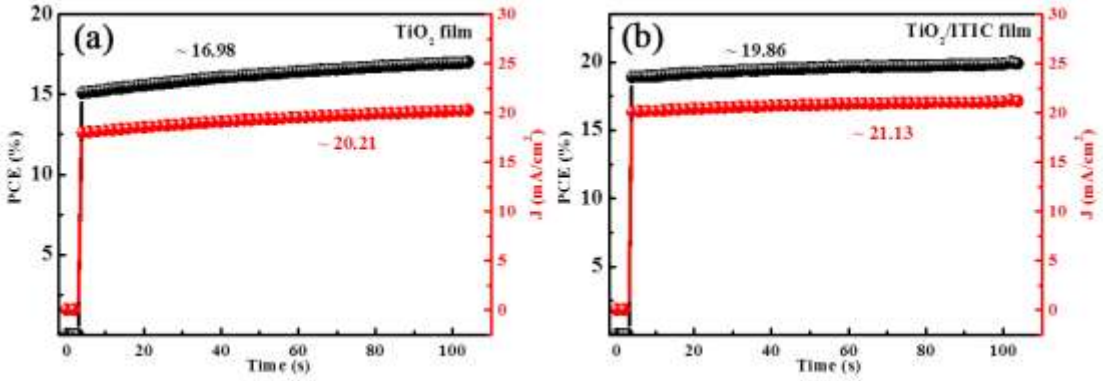

Figure S8. PCE measured as a function of time for the cells biased at 0.84 V for (a) TiO_2 ETL and 0.94 V for (b) ITIC modified TiO_2 ETL.

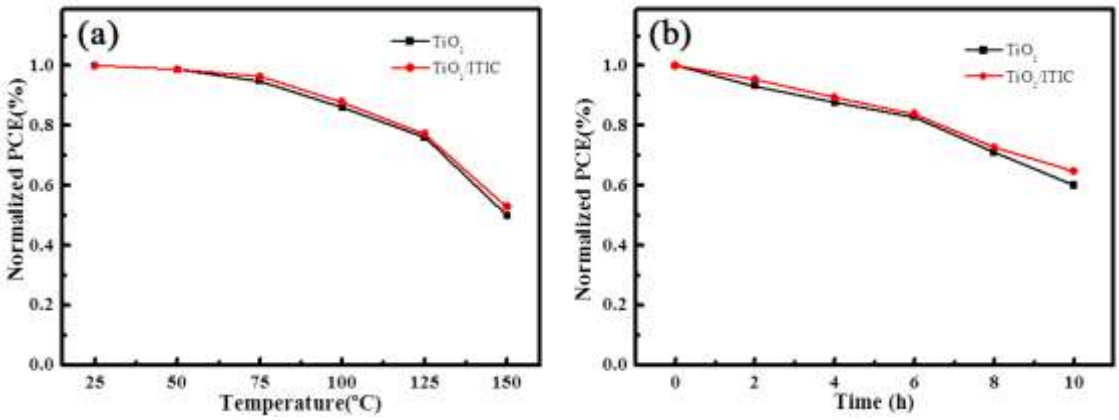

Figure S9. Normalized PCEs of PSCs with or without ITIC modified TiO_2 ETL: (a) after annealing different temperature for 10 min and (b) after annealing at 80 ^{o}C for different times.

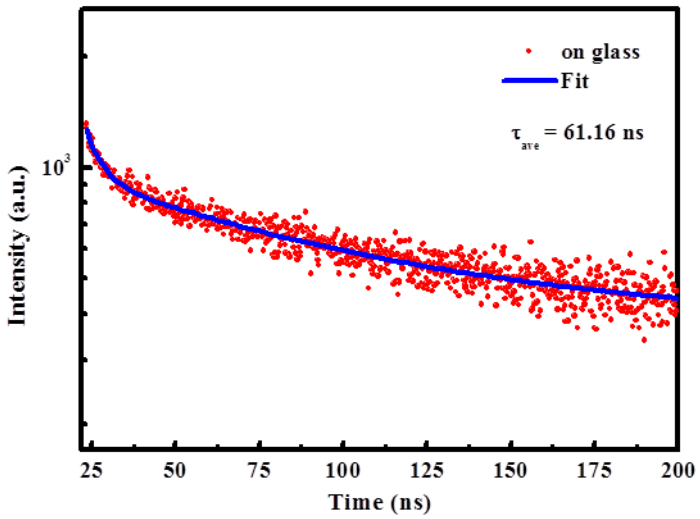

Figure S10. TRPL spectrum of perovskite deposited on glass substrate.

Table S1. EIS parameters for the PSCs with TiO_2 ETL and TiO_2/ITIC ETL.

Buffer layer	R_s (Ω)	R_{tr} (Ω)	R_{rec} (Ω)	C_{tr} (F)	C_{rec} (F)
TiO_2	30	190	1350	5.2×10^{-8}	2.0×10^{-7}
TiO_2/ITIC	25	300	2800	2.4×10^{-8}	1.1×10^{-7}

Table S2. Parameters of the TRPL spectra based on PSCs with TiO_2 ETL and TiO_2/ITIC ETL.

Buffer layer	τ_{ave} (ns)	τ_1 (ns)	τ_2 (ns)	% of τ_1	% of τ_2
TiO_2	47.83	67.45	9.28	21.28	78.72
TiO_2/ITIC	17.04	34.93	7.07	10.02	89.98