Supplementary Information

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Addressing the light-soaking issue in inverted organic solar cells using chemical bath deposited fluorinated TiO_x electron transport layer

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Rough Calculation of outdoor light soaking (Based on Singapore weather information)

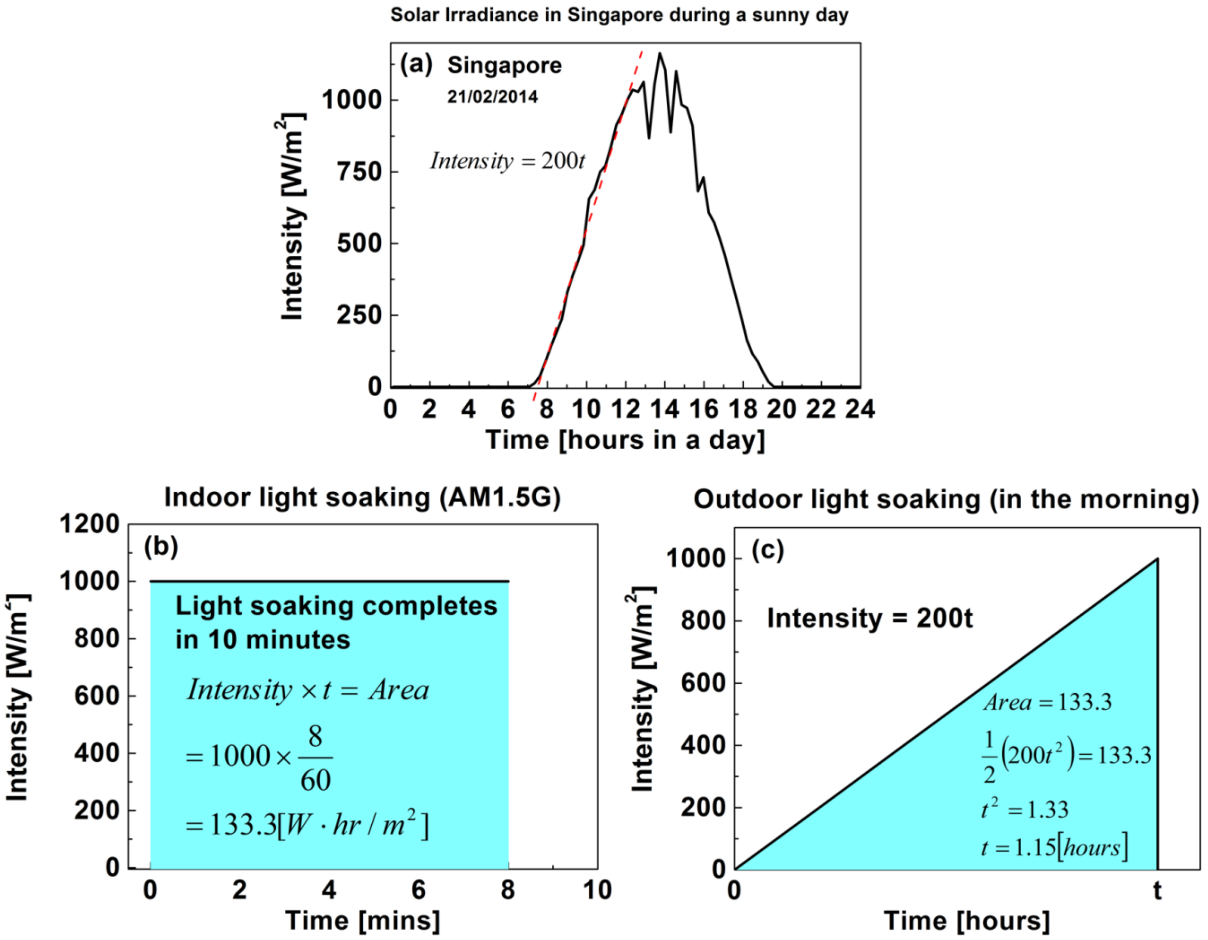

Figure S1 (a) Typical solar irradiance at function of time for a typical sunny day at Singapore; (b) Indoor light soaking calculation with assumption of 10 minutes of light soaking time; (c) Outdoor light soaking calculation by equating the area obtained from (b) and calculate the corresponding light soaking time required.

Assumptions:

(1) 100% conversion of photon to electron in solar cells

(2) Intensity is proportional to the number of photons, and proportional to the light soaking time. [i.e. Intensity $\propto$ Photon density $\propto$ Electron density $\propto$ time]

(3) Identical irradiance wavelength spectrum between indoor and outdoor

(4) Same area of device is used

We found that if a device requires 8 minutes of light-soaking treatment, it would require **at least, if not more than, 1 hour 10 minutes** of light-soaking in outdoor applications. Note that this treatment has to be done *every morning* throughout the entire lifetime of the device.

Optimization of precursor concentration of chemical bath deposited F-TiO_x

The concentration of $(NH_4)_2TiF_6$ was varied from 0.01M to 0.2M while keeping the concentration of H_3BO_3 fixed at 0.2 M at bath temperature of 40˚C. The resulting thickness and deposition rate of F-TiO_x are summarized in Figure S2 and Table S1. When the $(NH_4)_2TiF_6$ concentration is low (0.01 M - 0.02 M), the film growth is non-linear, and the film thickness saturates at 40 nm after 1 hour and 80 nm after 2 hours, respectively. F-TiO_x film forms at the initial reaction due to F- scavenging action by H_3BO_3 but subsequently halts due to inadequate TiF_6^{2-} ions for F-TiO_x formation. The deposition rate increases as $(NH_4)_2TiF_6$ concentration increases from 0.01 M to 0.05 M, and gradually decreases as the precursor concentration further increases. The highest deposition rate of 65 nm/h occurs at 0.05 M $(NH_4)_2TiF_6$ and 0.2 M H_3BO_3. When the concentration is increased, the rate of TiO_x film formation will decrease due to low F^- scavenging rate caused by a lesser amount of BO_3^{3-} ions, which will shift the reaction equilibrium (reaction (c)) to the left. Since the desired thickness for electron transport layer of OSC ranges from 20 to 130 nm [1-4], $(NH_4)_2TiF_6$ with concentration between 0.05 M to 0.15 M is of particular interest.

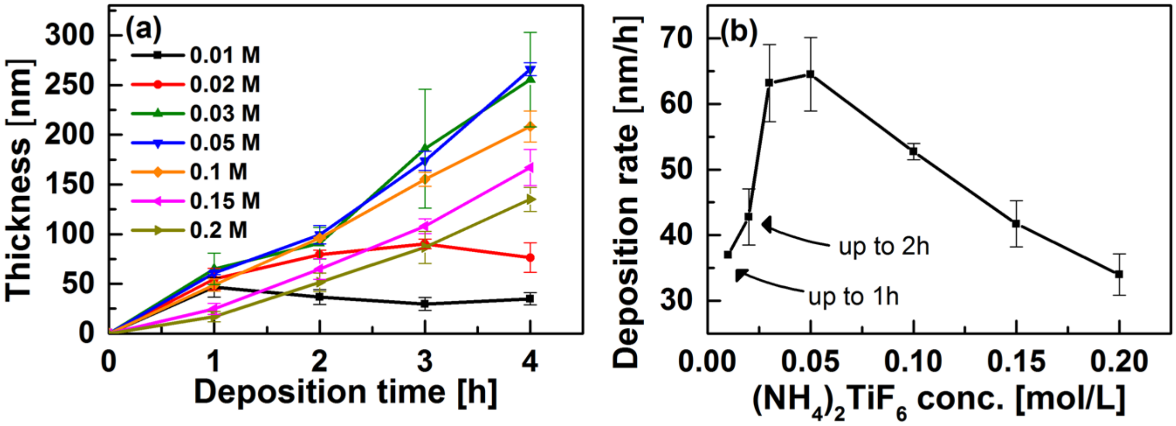

Figure S2 (a) Deposition thickness over 4 hours and; (b) Deposition rate of deposited TiO_x under various Ti precursor concentration and fixed 0.2 M H_3BO_3 concentration at a bath of 40˚C

Table S1 Growth of the chemical bath deposition with various $(NH_4)_2TiF_6$ concentration and fixed 0.2 M of H_3BO_3 at 40°C

Conc. of $(NH_4)_2TiF_6$ (M)	Conc. of H_3BO_3 (M)	Deposition rate (±5 nm h^{-1})	Remarks
0.01	0.2	37	Saturates after 1 h
0.02		43	Saturates after 2 h
0.03		63	Linear growth
0.05		65	
0.1		53	
0.15		42	
0.2		34	

By correlating the deposition rate and the morphology, two conclusions can be made. The optimal concentrations for the precursors are 0.1 M of $(NH_4)_2TiF_6$ and 0.2 M of H_3BO_3. In this concentration regime, both the desired morphology and the thickness can be achieved to produce an efficient ETL for IOSC device with minimal recombination losses.

XRD spectra

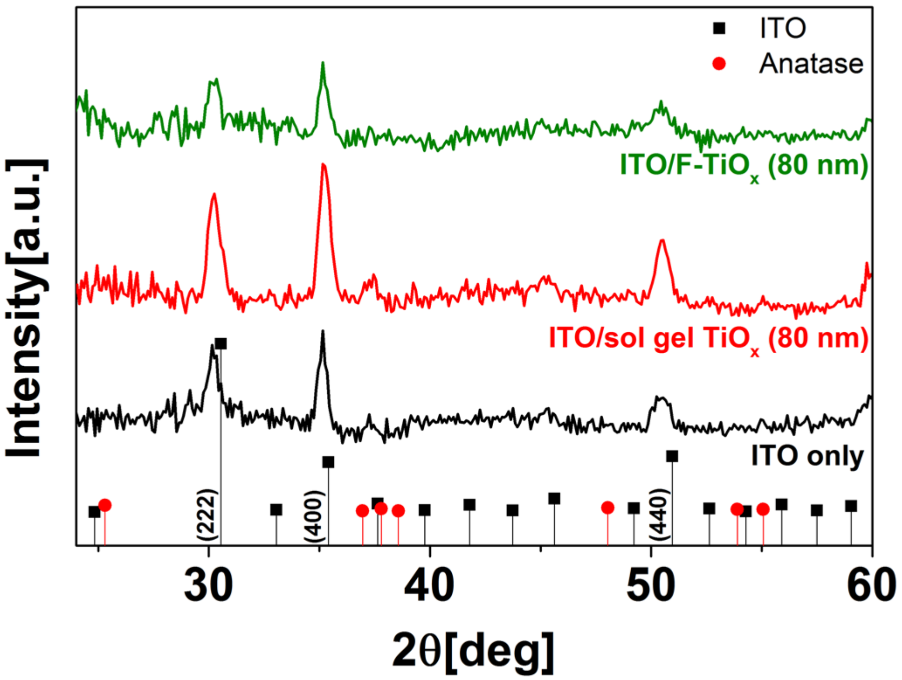

Figure S3 XRD spectra of ITO only (black), sol-gel coated TiOx (80 nm) on ITO (red) and chemical bath deposited F-TiO$_x$ (80 nm) on ITO (green). The peaks only show presence of ITO, implying the deposited TiO$_x$ films, regardless of sol-gel or chemical bath deposition, are amorphous.

Tauc plot for estimation of bandgap energy

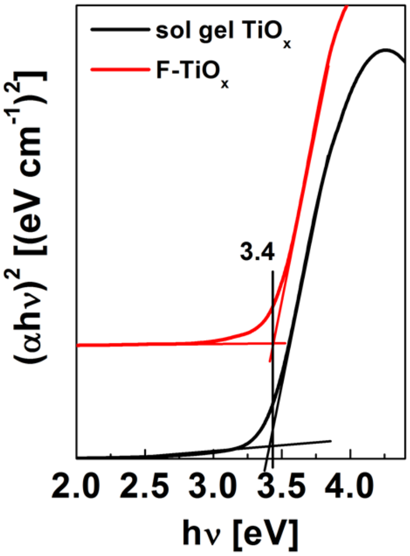

Figure S4 Tauc plot from the respective absorption spectra for sol-gel TiO$_x$ (0 % F conc., black), as-prepared F-TiO$_x$ (1.3 % F conc., red. The estimated bandgap energy (3.4 eV) was used to estimate the conduction band (CB) for band diagram construction.

Fitting function for calculating light soaking time

The light soaking time (τ_{soak}) was determined by fitting the experimental data in Figure 4(c) with a logistic function shown in Equation S1. The fitting was done using Origin Pro 9.0. The fitted parameters were tabulated in Table S2. τ_{soak} was then obtained by defining $PCE(\tau_{soak}) = 0.95PCE_{\max}$ and mapped back to the experimental data of Figure 4(c).

$$PCE(t) = \frac{A_0 - A_1}{1 + (t/\tau_0)^p} + A_1 \qquad \text{S1}$$

Table S2 Fitting parameters of various TiO$_x$ in inverted organic solar cells based on equation S1.

Electron transport layer	F at %	A_0	A_1	τ_0	p	τ_{soak}
Sol-gel TiO$_x$	0	0	1.0	89	1.8	450
CBD F-TiO$_x$ (as prepared)	1.3	0	1.0	11	2.5	35
CBD F-TiO$_x$ (NaOH treated)	1.5	0	1.0	175	2.8	520
CBD F-TiO$_x$ (H_2O treated)	1.7	0	1.0	27	2.1	110

References

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