Supporting Information

Hollow nanostructured rutile TiO_2 electron transporting layer via etching process for efficient perovskite solar cells: Impact of TiO_2 structural and crystalline properties

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Figure S1 Effect of etching time on TiO_2 nanorods. The etching time was varied from 0h (as deposited) to 4h. The etching temperature was 150°C.

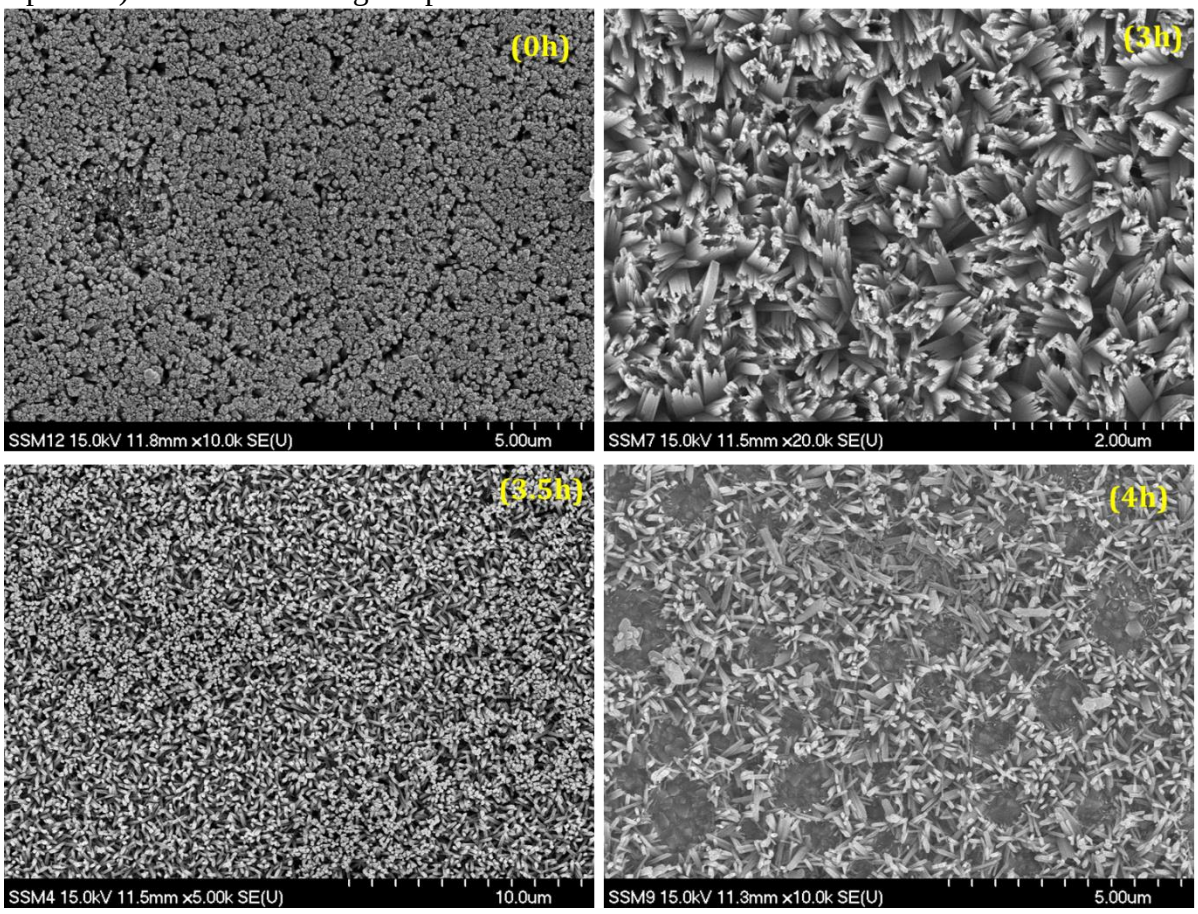

Figure S2 Cross sectional FESEM images of TiO_2 nanorods deposited at diferent concentration: (a-c) 240µl, (d-f) 220µl (g-i) 200µl TTIP.

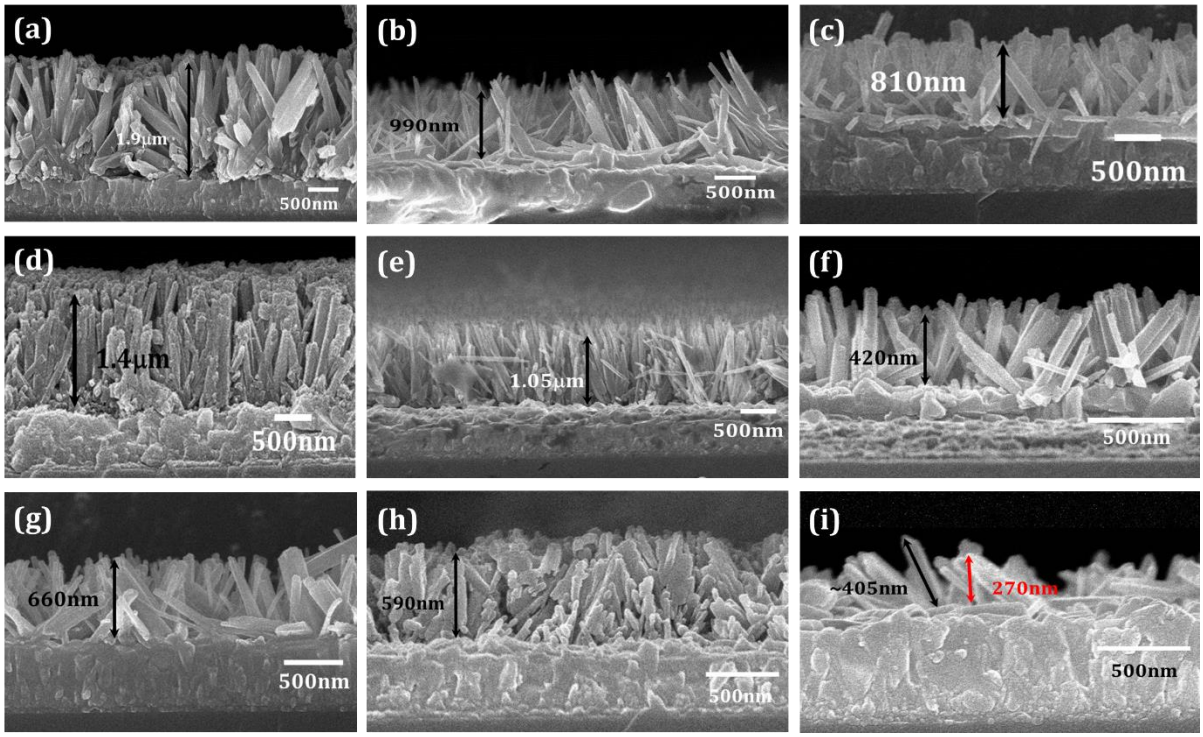

Figure S3 Cross sectional FESEM images of TiO_2 nanorods deposited at 180°C and etched at 150°C. (a-c) 160 µl (d-f) 180 µl (g-i) 200 µl (j-l) 220µl TBT precursor and etched at 0, 3.0 and 3.5h respectively. (*Note: Inset notation shows etching hours*)

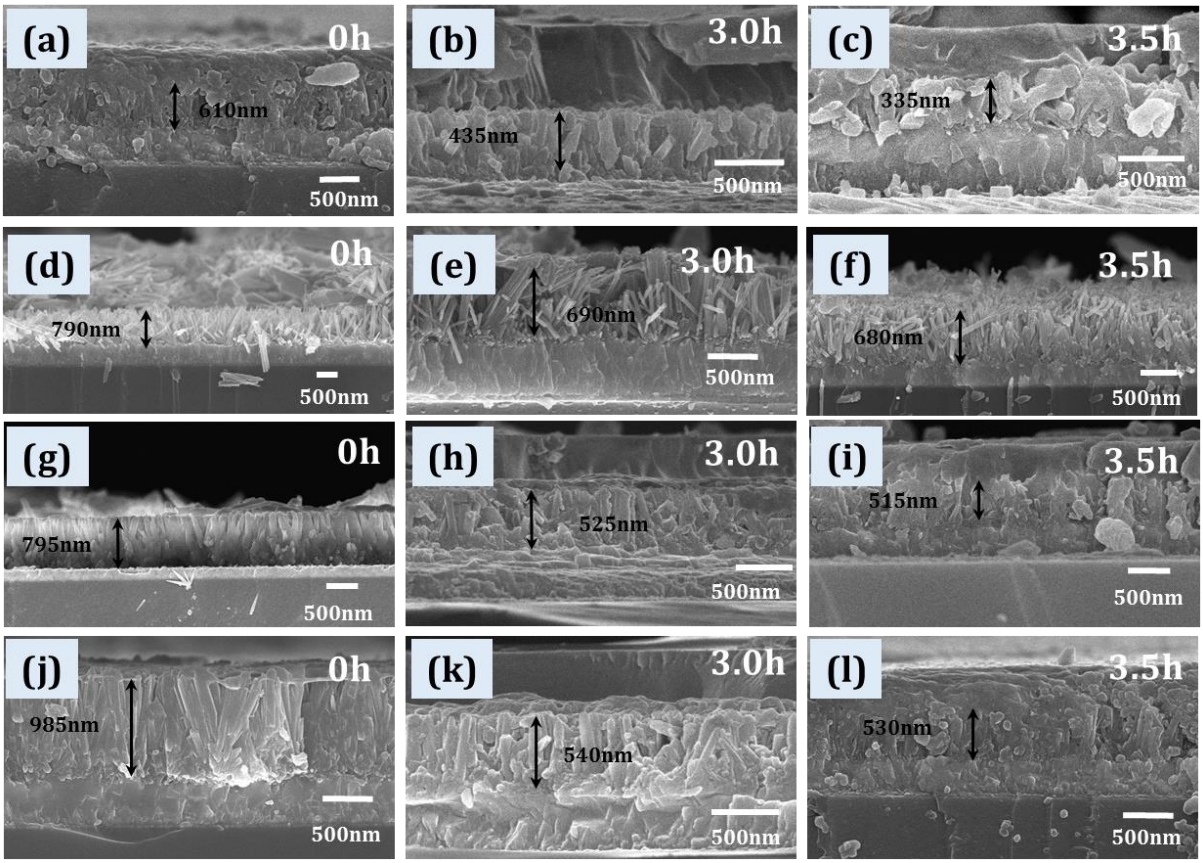

Figure S4 Schematic representation of formation of hollow and splited (solid) TiO_2 nanorods.

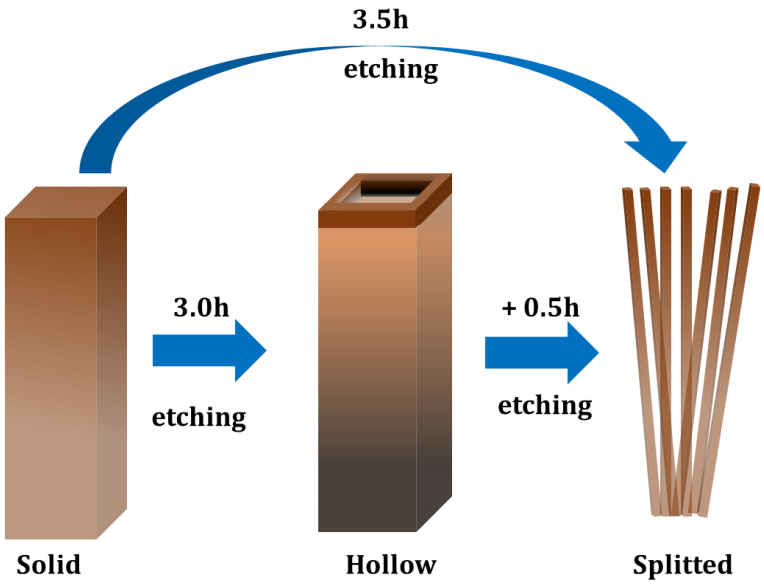

Figure S5 current density–voltage of perovskite solar cells based on TiO_2 nanorods and nanoflowers etched at different time (a) etched nanorods (b) etched TiO_2 nanorods from Titanium Butoxide (TBT) precursor (c) TiO_2 nanowires from TBT precursor (d) TiO_2 nanoflowers from TBT precursor. The J-V characteristics measured under AM 1.5G condition with input solar power Pin of 100mWcm^{-2} in reverse scan mode.

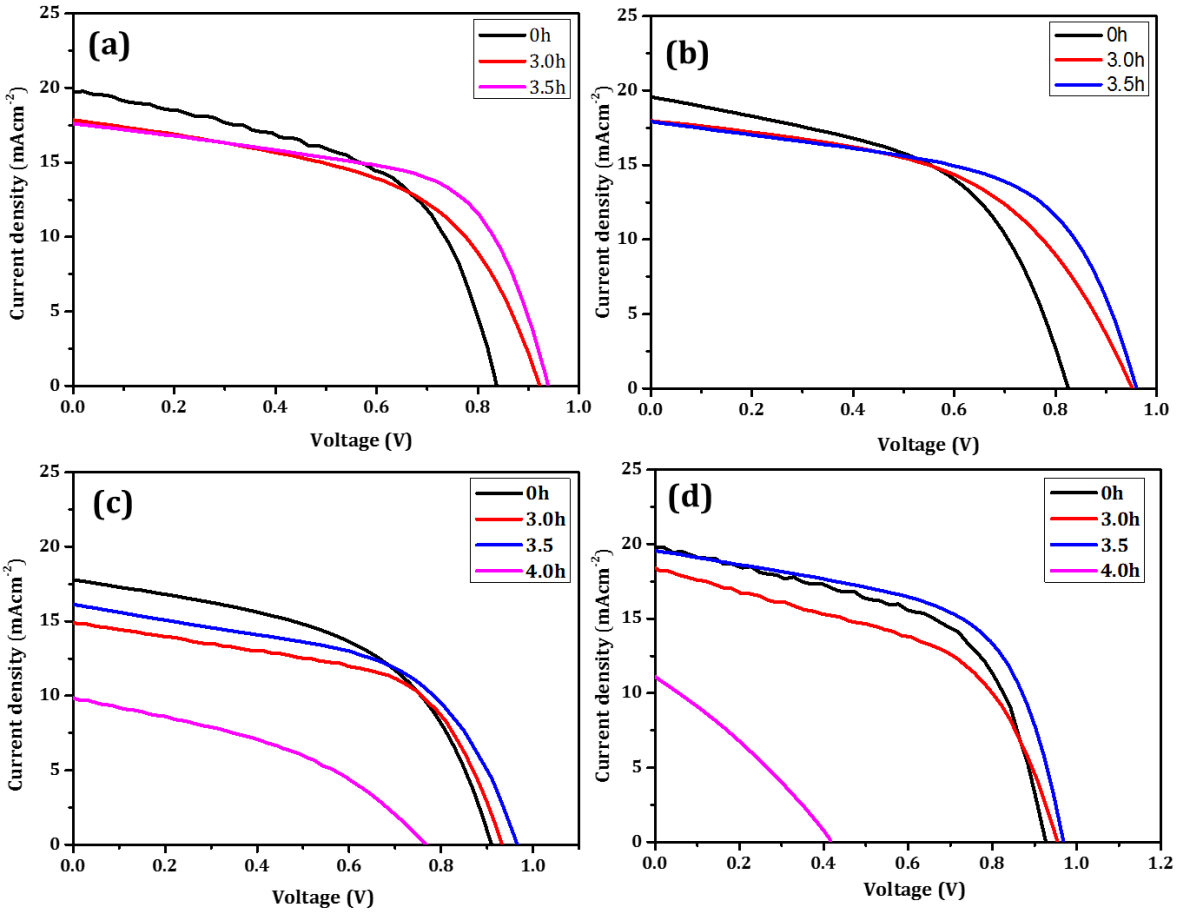

Figure S6 Cross sectional FESEM images of frbricated devices: Device configuration FTO/Bl-TiO_2/ TiO_2 (NS)*+$MAPbI_3$/PTAA/Au.

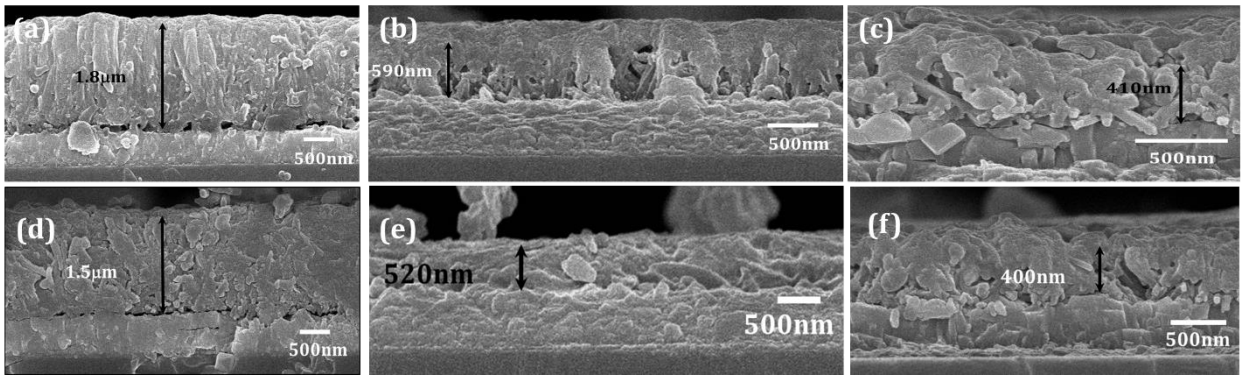

Figure S7 (a) Typical Cross Section micrograph of perovskite solar cell based on mp-TiO_2. Device configuration FTO/Bl-TiO_2/mp-TiO_2+$MAPbI_3$/PTAA/Au (Please note that Au contact is not shown in this cross section.)

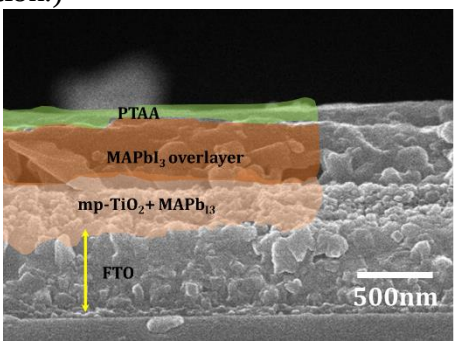

Figure S7(b) Photovoltaic performance of perovskite solar cells based on mp-TiO_2 measured by forward and reverse scans with 10mV voltage steps and 50ms delay times under AM 1.5 G illumination. Device configuration FTO/Bl-TiO_2/mp-TiO_2 + $MAPbI_3$ /spiro-MeOTAD/Au.

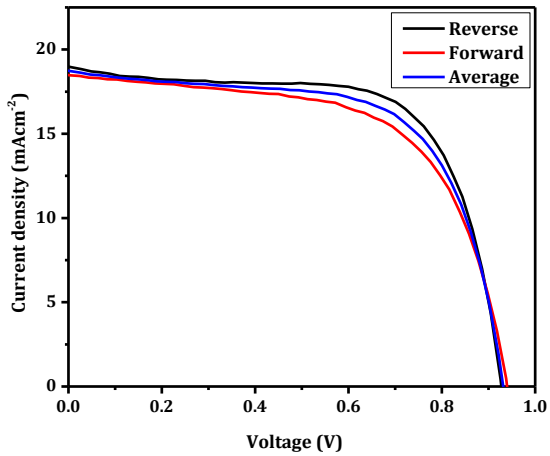

Figure S7(c) Photovoltaic performance of perovskite solar cells based on mp-TiO_2 measured by forward and reverse scans with 10mV voltage steps and 50ms delay times under AM 1.5 G illumination. Device configuration FTO/Bl-TiO_2/ mp-TiO_2+$MAPbI_3$/PTAA/Au.

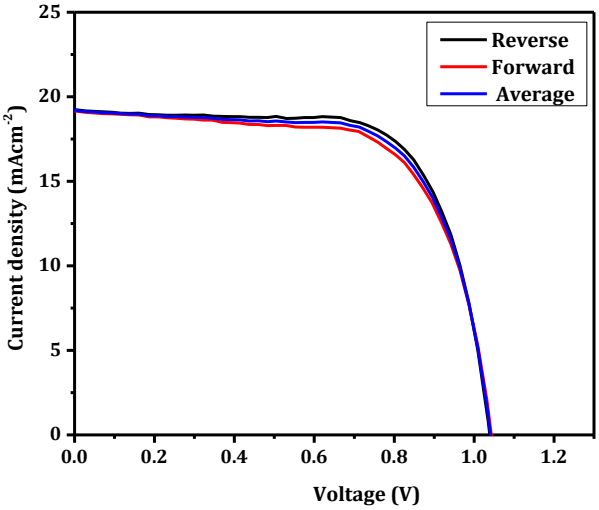

Figure S8 (a) Steady-state Photoluminescence (PL) spectra of the $MAPbI_3$, $MAPbI_{3-x}Cl_x$ and $(FAPbI_3)_{0.85}(MAPbBr_3)_{0.15}$ thin films deposited on etched TiO_2 (b) respective TRPL spectra

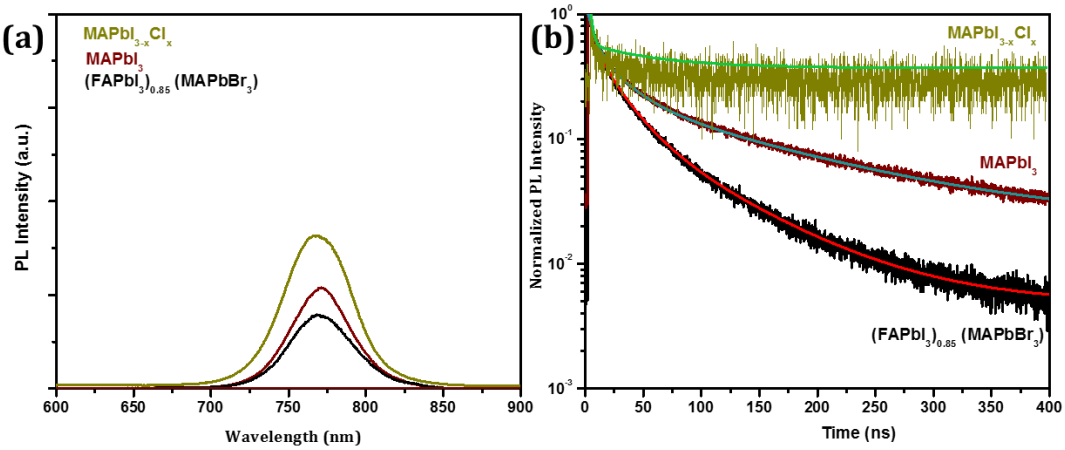

Table S1 Study of TTIP concentration in 20 ml ($HCl:H_2O$) solution hydrolyzed at 180C for 3 h and etched at different time interval.

Solution concentration (µl)	Deposition time (h)	Temp. (°C)	Nanorod length (µm ±0.01)	Etching time (h) at 150°C	Nanorod length (µm ±0.01)
100	3	180	No deposition	No deposition	No deposition
120	3	180	No deposition	No deposition	No deposition
140	3	180	0.450	0	0.450
	3	180	0.450	3	Detached
160	3	180	0.530	0	0.350
	3	180	0.530	3	Detached
	3	180	0.530	3.5	Detached
	3	180	0.530	4	Detached
180	3	180	0.610	0	0.685
	3	180	0.610	3	0.435
	3	180	0.685	3.5	0.335
	3	180	0.685	4	~0.100*
200	3	180	0.795	0	0.525
	3	180	0.795	3	0.525
	3	180	0.795	3.5	0.515
	3	180	0.795	4	~0.100*
220	3	180	0.985	0	0.985
	3	180	0.985	3	0.540
	3	180	0.985	3.5	0.530
	3	180	0.985	4	Detached
240	3	180	1.200	0	1.2
	3	180	1.200	3	0.950
	3	180	1.200	3.5	0.800
	3	180	1.200	4	Detached

**It is very difficult to measure the thickness of randomly oriented TiO_2 nanorods, therefore we have mentioned average value for these samples.*

Table S2 Solar Cell performance of optimized perovskite solar cells based on bare and etched TiO_2 nanostructures (<1μm length) tested under 1.5AM illumination (100 $mWcm^{-2}$). Etching temperature : 150°C for all samples.

Sample	Etching time (hr)	TiO_2 Thickness (nm ±5nm)	V_{OC} (V)	J_{SC} ($mAcm^{-2}$)	FF	η (%) (The average variation %)
TiO_2 nanorods (TTIP)	0	985	0.837 ±0.02	19.65 ±1.10	0.58 ±0.03	9.54 (8.8-9.6)
	3.0	540	0.923 ±0.01	17.87 ±0.70	0.61 ±0.02	10.02 (9.5-10.1)
	3.5	530	0.941 ±0.01	17.60 ±0.55	0.65±0.02	10.76 (10.4-10.8)
	4.0	0*	-	-	-	-
TiO_2 nanorods (TTIP)	0	795	0.824 ±0.01	19.59 ±0.85	0.59 ±0.02	9.52 (9.0-9.6)
	3.0	525	0.949 ±0.01	18.03 ±0.70	0.60 ±0.02	10.26 (9.9-10.4)
	3.5	515	0.960 ±0.01	17.86 ±0.35	0.65 ±0.02	11.15 (10.8-11.2)
	4.0	0*	-	-	-	-
TiO_2 nanorods (TBT)	0	790	0.911 ±0.02	17.86 ±0.65	0.57 ±0.02	9.27 (9.0-9.4)
	3.0	690	0.930 ±0.02	16.14 ±0.70	0.62 ±0.04	9.46 (9.0-9.5)
	3.5	680	0.968 ±0.02	14.95 ±0.60	0.65 ±0.03	9.41 (8.8-9.6)
	4.0	~100[¥]	0.770 ±0.03	9.88 ±2.50	0.39 ±0.08	2.97 (1.5-4.5)[£]
TiO_2 nanoflowers/nanowires[€] (TBT)	0	610	0.926 ±0.01	19.88 ±0.50	0.62±0.02	11.41 (11.0-11.5)
	3.0	435	0.955 ±0.01	18.38 ±0.40	0.65 ±0.03	11.41 (10.7-11.5)
	3.5	335	0.969 ±0.01	19.56 ±0.30	0.68±0.02	12.89 (11.6-13.1)
	4.0	~100[¥]	0.415 ±0.04	11.10 ±1.25	0.21 ±0.10	0.97 (0.1-1.0)[£]

*****_ETL free device. In this device all TiO_2 nanorods/nanoflowers are detached from FTO substrate, therefore we did not fabricated devices for these conditions._ [¥] _This is average thickness of the device. However, this is not accurate thickness, since if we check the low magnification of these sample then all nanorods/nanowires are randomly oriented and circular patched were observed (Figure S7, etched 4h)_ [€] _In our experiment, the TiO_2 nanorods are deposited at low concentration show nanowire like morphology instead of nanoflowers._ [£] _We observed the major variation in these devices._