

Electronic Supplementary Information

**Graphene Nanoparticles Decorated Silicon Nanowires with Tungsten Oxide Counter  
Electrode for Quasi Solid-State Hybrid Solar Cells**

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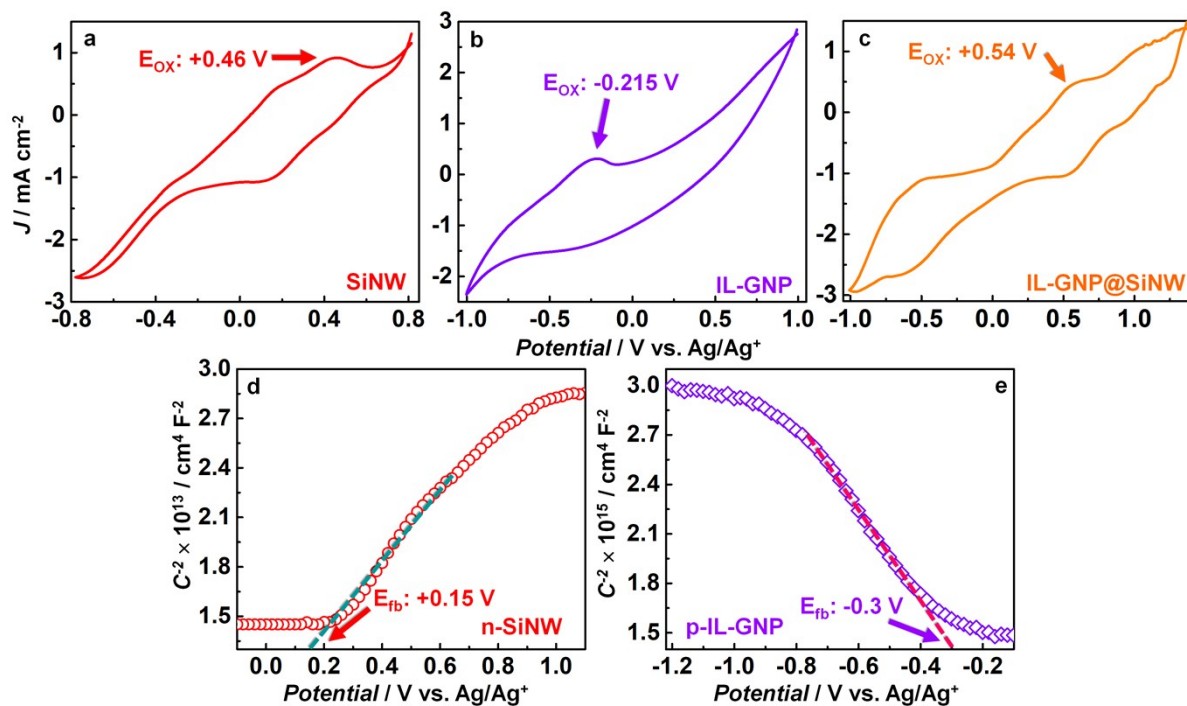


Figure S1 CV plots of (a) SiNW, (b) IL-GNP and (c) IL-GNP@SiNW in three electrode cells, with 0.1 M KCl as the electrolyte, a Pt rod as the counter electrode and Ag/AgCl/KCL as the reference. Mott-Schottky plots of (d) SiNW and (e) IL-GNP in the same cell configuration in dark. The intercepts are the flat band potentials in (d) and (e).

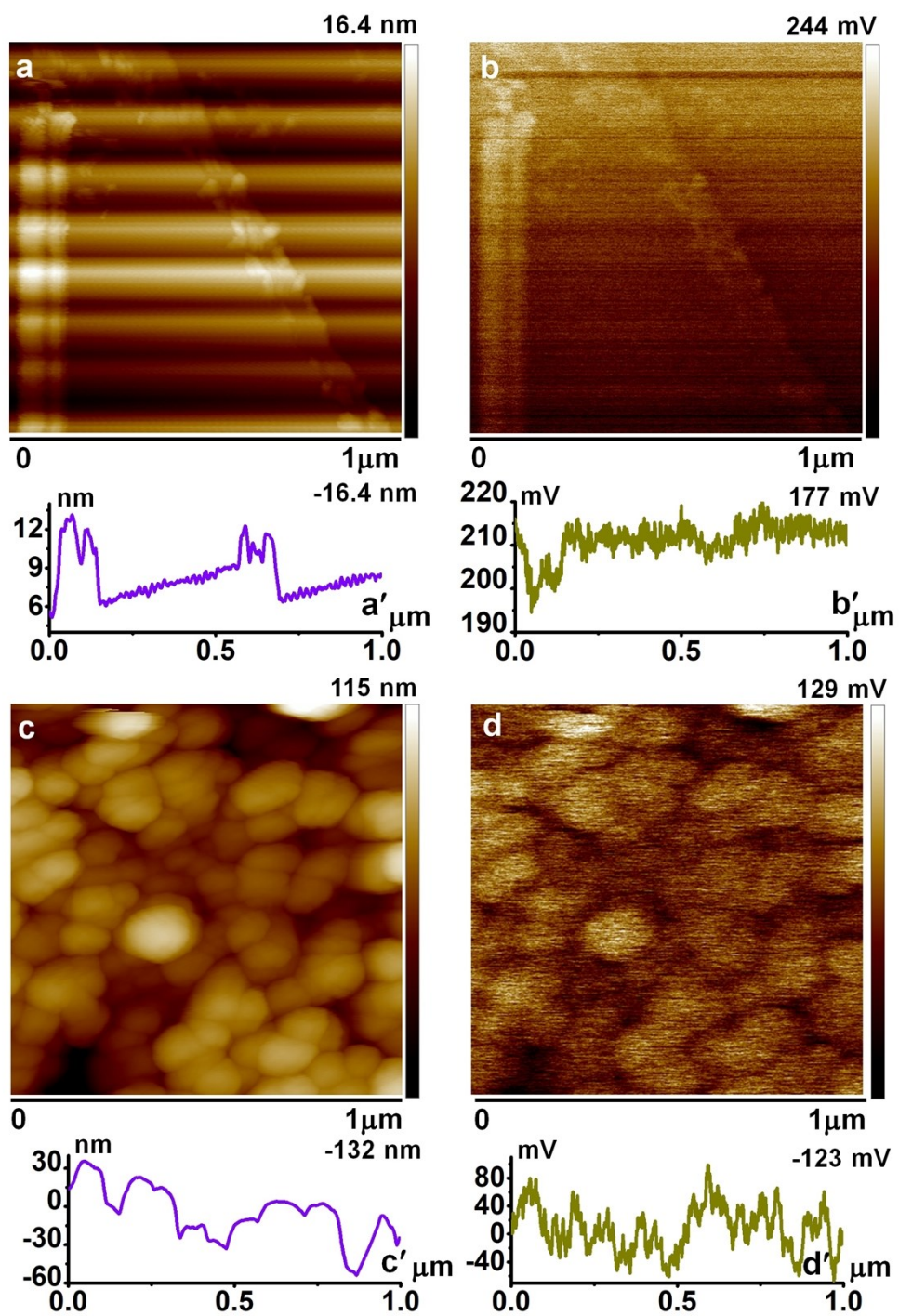


Figure S2 Topography (a,c) and surface potential maps (b,d) of HOPG and  $\text{WO}_3$ , and the corresponding representative section profiles are shown in (a',c') and (b',d') respectively.

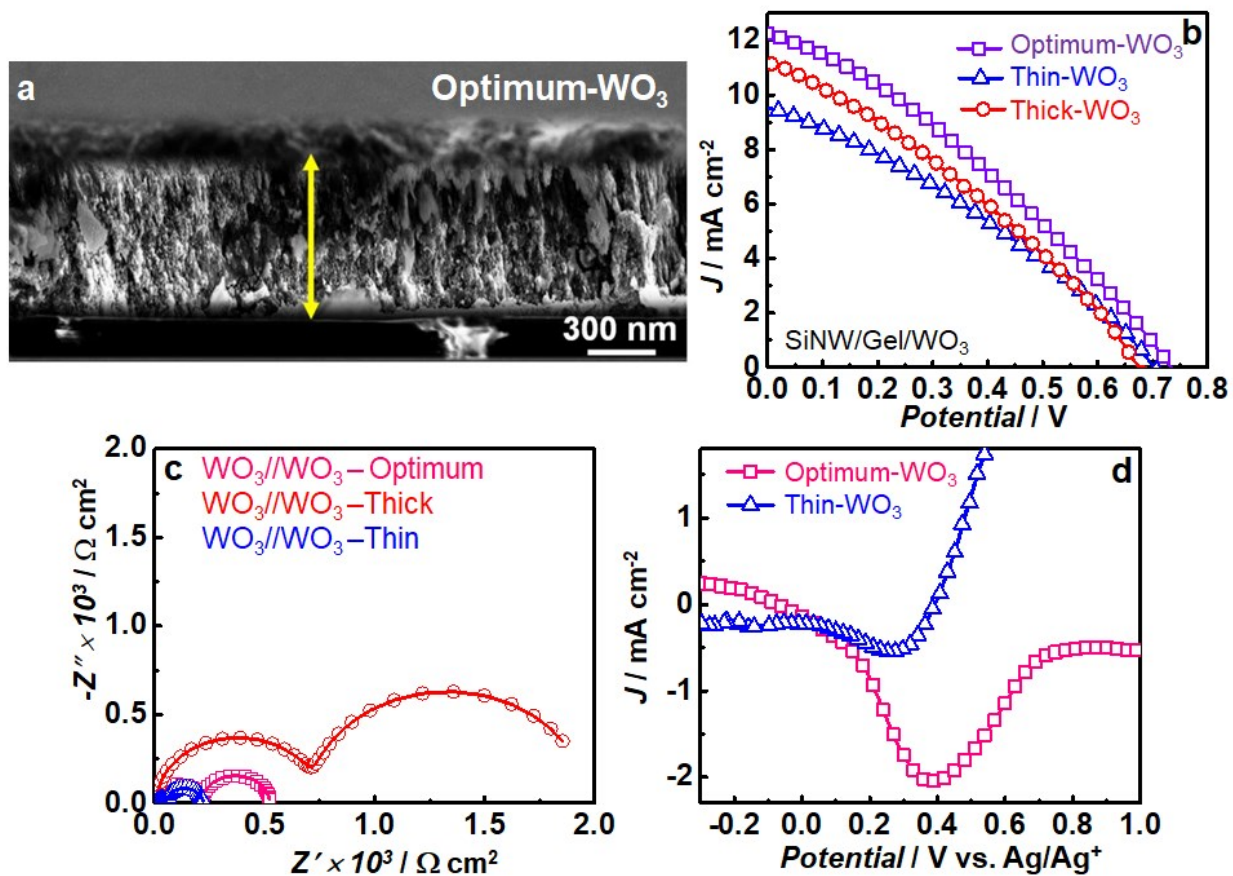


Figure S3 (a) Cross-sectional SEM image of a WO<sub>3</sub>@FTO film. (b) J-V characteristics of SiNW/gel/WO<sub>3</sub> cells, with varying WO<sub>3</sub> thicknesses, based on electrodeposition span. (c) Nyquist plots compared for symmetric cells of WO<sub>3</sub> (of different thicknesses) with BMIM<sup>+</sup>I<sub>2</sub> gel over 10 mHz to 1 MHz. (d) I-V plots comparing the tri-iodide reduction capability of WO<sub>3</sub> films of different thicknesses, with Pt as the counter electrode.

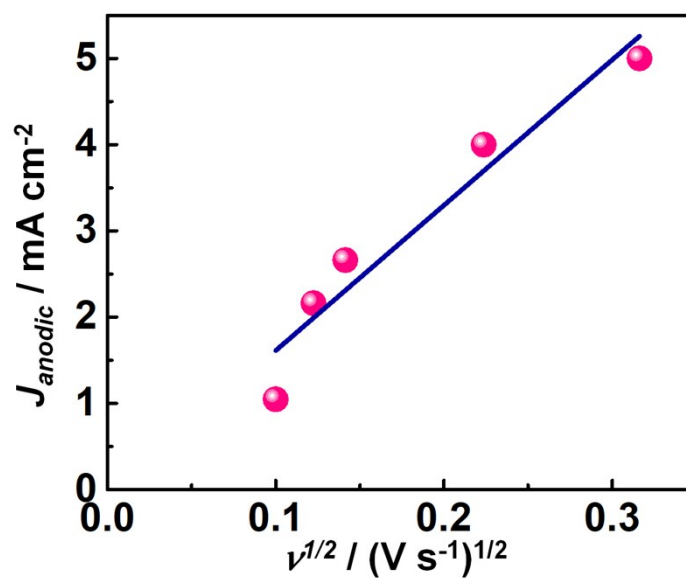


Figure S4 Linear dependence of anodic peak current density versus square root of scan rate for a  $\text{WO}_3$  film.

Table S1 Fitted parameters for Nyquist plots for symmetric cells based on the gel electrolyte composed of 1 M BMIM<sup>+</sup>I<sup>-</sup>, 0.05 M I<sub>2</sub>, 2 wt% poly(AMPS) and 7 wt% SiO<sub>2</sub> in PC.

Cell	$R_1$ ( $R_{\text{gel}}, \Omega$ $\text{cm}^2$ )	$R_2$ ( $R_{\text{electron}}, \Omega$ $\text{cm}^2$ )	$R_3$ ( $R_{\text{ct}}, \Omega \text{ cm}^2$ )	$C_2$ ( $C_{\mu}, \text{F cm}^2$ )	$C_3$ ( $C_{\text{dl}}, \text{F cm}^2$ )
FTO/ $\text{WO}_3$ // $\text{WO}_3$ /FTO	6.3	206.2	312.5	$1.2 \times 10^{-5}$	$3.4 \times 10^{-3}$
FTO//FTO	10.6	33.2	4286	$3.6 \times 10^{-5}$	$2 \times 10^{-3}$

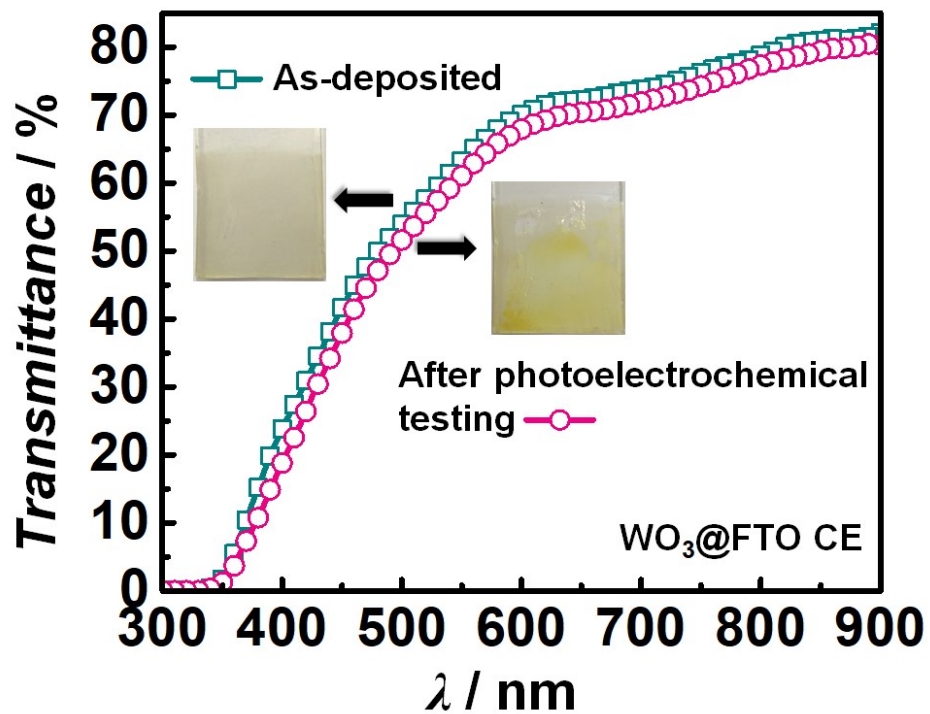


Figure S5 Transmittance spectra of a  $\text{WO}_3$  CE film before and after the solar cell stability test.

Table S2 Solar cell parameters for different cells, standard deviation on 5-cell data.

Cells	V <sub>OC</sub> (mV)	J <sub>SC</sub> (mA cm <sup>-2</sup> )	FF	PCE (%)
SiNW/Gel/WO <sub>3</sub>				
Cell 1	754	13.62	0.461	4.73
Cell 2	644	12.19	0.427	3.35
Cell 3	674	12.37	0.436	3.64
Cell 4	704	12.91	0.445	4.05
Cell 5	724	13.19	0.451	4.31
Average	700±43	12.86±0.59	0.444±0.013	4.02±0.54
SiNW/Liquid/WO <sub>3</sub>				
Cell 1	731	12.22	0.316	2.83
Cell 2	631	10.60	0.296	1.98
Cell 3	661	11.02	0.301	2.19
Cell 4	691	11.42	0.308	2.43
Cell 5	701	11.70	0.310	2.54
Average	683±38	11.39±0.62	0.306±0.008	2.39±0.33
IL-GNP@SiNW/Gel/WO <sub>3</sub>				
Cell 1	768	18.39	0.562	7.93
Cell 2	753	17.32	0.558	7.28
Cell 3	740	17.92	0.557	7.38
Cell 4	738	17.25	0.556	7.08
Cell 5	718	16.75	0.551	6.63
Average	743±19	17.53±0.64	0.557±0.004	7.26±0.47
IL-GNP@SiNW/Liquid/WO <sub>3</sub>				
Cell 1	761	17.23	0.487	6.39
Cell 2	683	15.83	0.462	5.00
Cell 3	673	15.39	0.459	4.76
Cell 4	733	16.36	0.477	5.72
Cell 5	703	16.16	0.468	5.32
Average	711±36	16.19±0.69	0.471±0.011	5.44±0.64

Table S3 Comparison of n-SiNW based solar cells from photovoltaic literature.

Solar Cell Architecture	$J_{sc}$ (mA cm <sup>-2</sup> )	$V_{oc}$ (mV)	FF	PCE or $\eta$ (%)	Reference
Al/p-Si-n-SiNW/TCO/polymer (0.6 cm <sup>2</sup> )	2	230-280	0.2	0.1	1
Glass/mc-p-Si/mc-n-SiNW/mc- n <sup>+</sup> -SiNW/Au (0.64 mm <sup>2</sup> )	40	450	-	4.4	2
PIN-RJSiNW	14.6	750	0.581	6.32	3
n-SiNW/p-SiNW/Al/Pd (8 $\mu$ m absorber)	16.82 $\pm$ 0.50	525 $\pm$ 2	0.559 $\pm$ 0.02	5.30 $\pm$ 0.19	4
p-i-n -coaxial SiNW (upper bound)	23.9 $\pm$ 1.2	260	0.55	3.4 $\pm$ 0.2	5
p-i-n -coaxial SiNW (lower bound)	16 $\pm$ 0.8	260	0.55	2.3 $\pm$ 0.2	5
ITO/V <sub>2</sub> O <sub>5</sub> /n-SiNW/TiO <sub>2</sub> /Al	35.7	490	0.727	12.7	6
ITO/n-SiNW/TiO <sub>2</sub> /Al	20.4	214	0.425	1.86	6
AZO core-shell TCO/a-Si/n- SiNW (7 mm <sup>2</sup> )	27	476	0.562	7.29	7
Al/n-SiNW/PEDOT/ITO	19.28	470	0.61	5.09	8
Al/n-SiNW/Spiro- OMeTAD/PEDOT:PSS/Ag	26.7	530	0.643	9.2	9
Al/n-SiNW- DADS/PEDOT:PSS/Ag	28.80 $\pm$ 1.03	488 $\pm$ 6	0.49 $\pm$ 0.012	7.02 $\pm$ 0.17	10
n-SiNW/40%HBr, 3%Br <sub>2</sub> /Pt mesh	0.872	730 $\pm$ 20	0.45	0.286	11
PtNPs/C@n-SiNW/8.6M HBr, 0.05Br <sub>2</sub> /Pt mesh	36.89	530	0.555	10.86	12
n-SiNW-CH <sub>3</sub> (Pt)/0.05 M I <sub>2</sub> , 0.1 M LiI in a mixed IL (EMISCN:PMII, 7:13, v/v)/Pt - ITO	33.7	322	0.40	4.3	13
n-SiNW-PtNPs/8.6M HBr, 0.05Br <sub>2</sub> /Pt	24.26	550	0.61	8.14	14
n-SiNW-AuNPs/8.6M HBr, 0.05Br <sub>2</sub> /Pt	14	745.3	0.23	2.4	14
Se NPs@Si NWs/8.6M HBr, 0.05Br <sub>2</sub> /C-fabric	17.12	790	0.52	7.03	15
C@TeNRs@Si NWs/8.6M HBr, 0.05Br <sub>2</sub> /C-fabric	23.27	893	0.56	11.59	16
IL-GNP@SiNW/I <sub>2</sub> ,I <sup>-</sup> gel/WO <sub>3</sub>	18.39	768	0.56	7.93	This work

TCO: Transparent conducting coating, mc: Multicrystalline, RJ: Radial junction, AZO: Al doped ZnO, a: Amorphous, Spiro-OMeTAD: 2,2',7,7'-Tetrakis-(N,N-di-4-methoxyphenylamino)-9,9'-spirobifluorene, ITO: In<sub>2</sub>O<sub>3</sub>:Sn coated glass, PEDOT: Poly(3,4-ethylenedioxythiophene), PSS: Poly(4-styrenesulfonate), DADS: Diallyl disulfide, IL: Ionic liquid, PMII: 1-Propyl-3-



methylimidazolium iodide, EMISCN: 1-Ethyl-3-methylimidazolium thiocyanate, NPs: Nanoparticles, IL-GNP: Ionic liquid functionalized graphene nanoparticles.

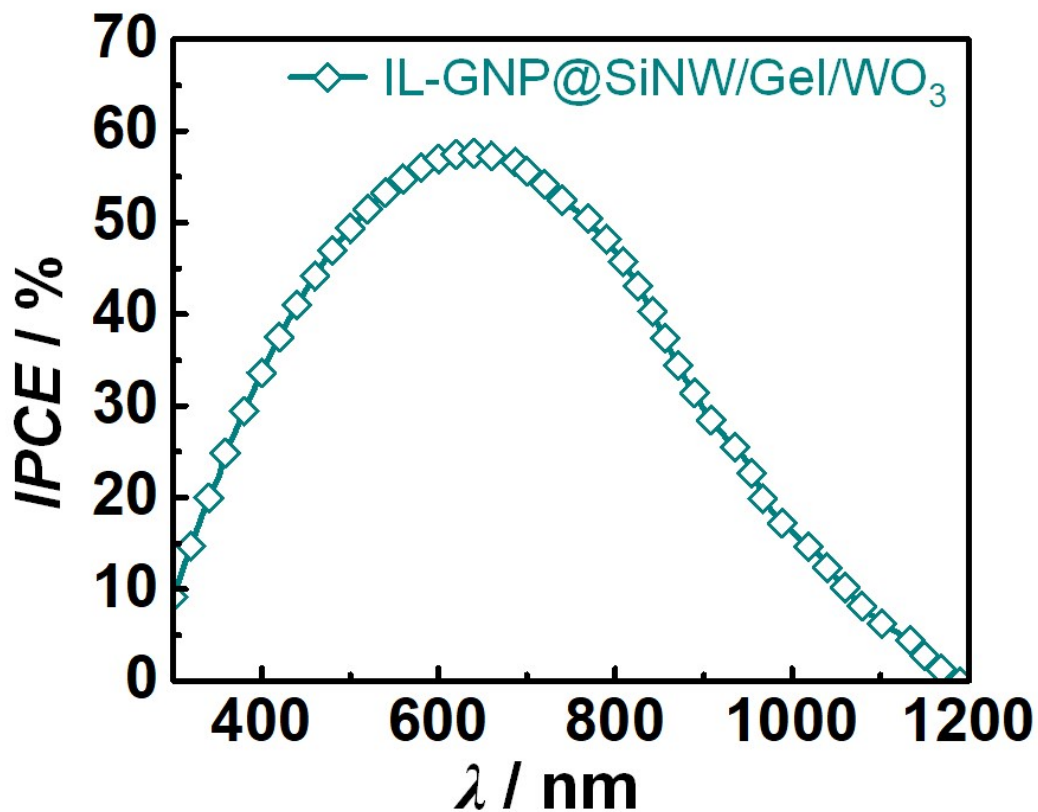


Figure S6 IPCE plot for the IL-GNP@SiNW/Gel/WO<sub>3</sub> hybrid solar cell.

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