Self-generation of a quasi p-n junction for high efficiency chemical-

doping-free graphene/silicon solar cells using a transition metal

oxide interlayer

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Supporting information



Figure S1. Work function of WO₃, Gr and n-Si measured by a Kelvin probe under ambient

conditions.



Figure S2. (a) Raman spectrum of monolayer Gr film measured on SiO₂/Si substrate and (b) light transmission spectrum of monolayer Gr film.



Figure S3. Schematic device structures of WO₃/Si solar cells (A), Gr/Si solar cells without (B) and with (C) a WO₃ interlayer.

Table S1. Summarized photovoltaic parameters of WO₃/Si solar cell (Device A), Gr/Si solar cells without (Device B) and with (Device C) a WO₃ interlayer.

Devices	$V_{\rm OC}({\rm mV})$	$J_{\rm SC}~({\rm mA/cm^2})$	FF (%)	PCE (%)
А	269.04	0.07	35.46	0.01
В	383.61	26.75	38.91	3.99
С	511.06	32.92	62.94	10.59

Device structures	V_{OC}	J_{SC}	FF	Pristine PCE	Doped PCE	Year
	(V)	(mA/cm^2)	(%)	(%)	(%)	
This work	0.51	32.9	63	10.59		2015
Gr/Si ¹	0.48	6.5	56	1.65		2010
Gr/Si ²	0.43	14.2	32	1.9	8.6	2012
Boron doped Gr/Si ³	0.53	18.8	23	2.3	3.4	2012
Gr/Si ⁴	0.43	16.2	39	2.66	5.47	2013
Gr/Si nanohole array ⁵	0.46	27.8	47	6.02	10.40	2013
Gr/Si ⁶	0.51	17.5	43	5.53		2013
Gr/P3HT/CH ₃ -Si nanowires ⁷	0.43	27.3	38	4.42	9.70	2013
Gr/Si ⁸	0.39	22.9	43	3.78	14.5	2013
Gr/GO/Si ⁹	0.45	26.6	52	6.18		2014
Gr/GO/Si ¹⁰	0.48	26.4	41	5.2	12.3	2014
Gr/MoS ₂ /Si ¹¹	0.50	28.1	47	6.56		2015
CNT/Gr/Si ¹²	0.54	22.7	57	7.97	14.88	2015
Gr/P3HT/ultrathin c-Si ¹³	0.54	22.9	41	5.06	8.26	2015
Gr/AgNWs/Al ₂ O ₃ /Si ¹⁴	0.53	29.2	56	8.68		2015
Crack-filled Gr with Au NP/Si ¹⁵	0.48	24.8	66	7.8	12.3	2015
TiO ₂ /Gr/SiO _x /Si ¹⁶					15.6	2015

Table S2. Selected representative results of Gr/Si solar cells before (including the photovoltaic

parameters) and after chemical doping.



Figure S4. Reflectance spectra of Si, WO3/Si, and Gr/WO3/Si solar cell (PMMA/Gr/WO3/Si).



Figure S5. PCE of a Gr/WO₃/Si solar cell exposed under ambient conditions.



Figure S6. Carrier density of Gr under ambient condition and covered by WO3 thin film measured

by Hall Effect.

Table S3. Performances degradation of $Gr/WO_3/Si$ solar cells after PMMA removing process. The annealing temperature to remove the PMMA coating should be larger than 400 °C, while a mild annealing (150 °C) has already reduced PCE to lower than 5%.

Post-treatment	$V_{OC} (\mathrm{mV})$	J_{SC} (mA/cm ²)	<i>FF</i> (%)	PCE (%)
Dipping in acetone	444.16	5.42	12.90	0.31
	438.25	10.30	14.69	0.66
	372.04	9.45	16.43	0.58
Annealing at 150 °C	431.89	32.40	34.23	4.79
	399.42	31.04	30.22	3.75
	416.16	32.52	31.00	4.19

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