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Graphene oxide as a *p*-dopant and anti-reflection coating layer, in graphene/silicon solar cells

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1. Experimental Methods

N-type Silicon (0.5Ω -1Ωcm, 300µm), single side polished, wafer was covered with a 350 nm silicon oxide (SiO_2) layer via plasma enhanced chemical vapor deposition (PECVD). An active area of 9 mm² (3.0 x3.0 mm) window defined by photolithography, followed by titanium/gold (Ti/Au) (20 nm/150 nm) sputtered to provide a low resistance front contact for graphene. Aluminum (Al) was sputtered as a back contact (~200 nm) due to do lower work function compare to the Au. Buffer oxide etch (BOE) with HN_4F/HF (6:1) ratio was employed to remove the SiO_2 layer in active area for 10 minutes, followed by cleaning the chemical residues with deionized water (DI water), acetone, and isopropanol, respectively. Chemical Vapor Deposition (CVD) mono-layer graphene (MLG) on copper (Cu) foil bought from ACS Material.[1] PMMA spin coated on Gr/Cu foil for a mechanical support during the transfer of graphene. Cu foil was etched in 1M ammonium persulfate ($(NH_4)_2S_2O_8$) for 6 hours and free floating Gr/PMMA transferred in DI water to clean the graphene. Floating Gr/PMMA manually transferred on sample. Before graphene transfer, samples were stored in air for 5min, 15min, 30min, 45min, 1h, 2h, 4h, 6h to form the natural oxide layer which has recently shown to improve the efficiency of Gr/Si solar cell.[2] For our devices, the highest efficiency of the pristine sample (3.6%) were achieved after 30 minutes air storage and used as a reference for the preparation of new samples. After graphene transfer, samples were left in ambient air overnight to dry, followed by removing PMMA with acetone for 45 minutes. Samples were annealed 1 hour at 400°C under H_2/N_2 gas flow (10sccm) to improve the contact of Gr/Si junction.

GO was synthesized with the modified Hummer's method previously described in literature.[3] GO dispersed in DI water with a concentration of 1mg/mL. Well dispersed, highly stable GO solution spin coated on sample to obtain a uniform film of GO. By controlling the spin coating parameters, the optimum thickness (~200 nm) of the GO layer was determined from the highest efficiency of device.

J-V characteristic of devices were tested by a source meter (Keithley 2420) and a solar simulator (Newport 66905, 50-500 Watt, Xenon Lamp) under AM 1.5G at illumination intensity of 100 mW/cm^2, calibrated by a standard Si photo diode. The efficiency of device (η) which is the maximum power output of device (Figure S2), calculated from the following equation:

$$\eta = V_{oc} x J_{sc} x FF$$

Where V_{oc} is open circuit potential, J_{sc} is short current density, *FF* is fill factor.

Renishaw inVia (150W) Raman spectrometer with a laser excitation of 514 nm was used to obtain Raman spectrum after calibrated with an internal-Si wafer. Layer thicknesses of GO coating were measured with RUDOLPH AutoEL Ellipsometer and Dektak 150 Profilometer, and further confirmed with Philips JL30 ESEM (Figure S4). A monochromator (Newport, CS260) equipped with the solar simulator with the 1.5 AM filter as a light source was used to perform the external quantum efficiency (EQE) measurements. For our set up, the EQE ratio designed to observe the number of charge carriers collected in solar cell to the number of absorbed photons for a given energy at zero bias. Therefore the calculated current density should be comparable with observed $J_{sc.}$ The monochromatic light spectrum was calibrated by a silicon photodiode (Newport, 818-UV). J_{sc} values, from the EQE plot, calculated from the following equations:

$$\text{EQE} = \text{Collected Electron/Absorbed Photon}$$

$$J_{SC} = \int EQE(\lambda) \times E(\lambda) \times \lambda \times \frac{1}{1240} d\lambda$$

where EQE(λ) is as a function of λ, obtained from the measurement, $E(\lambda)$ is the standard solar spectrum, and λ is the wavelength.

Reflectance measurements were carried out using a Lambda 1050 UV/Vis/NIR Spectrophotometer. We have performed both diffuse reflectance (DR) and specular reflectance (SR) measurements to further confirm the anti-reflection effect of GO on samples. (Figure S5) Although GO/Gr/Si sample shows slightly higher (16%) reflectance for SR at 600 nm, it is still comparable with the DR measurements and both show similar characteristics. The lowest reflectivity for SR measurements is observed around 780 nm for both samples in agreement with highest EQE wavelength, which corresponds to 98 nm layer thickness, in agreement with the thickness measurements.

2. Figure S1

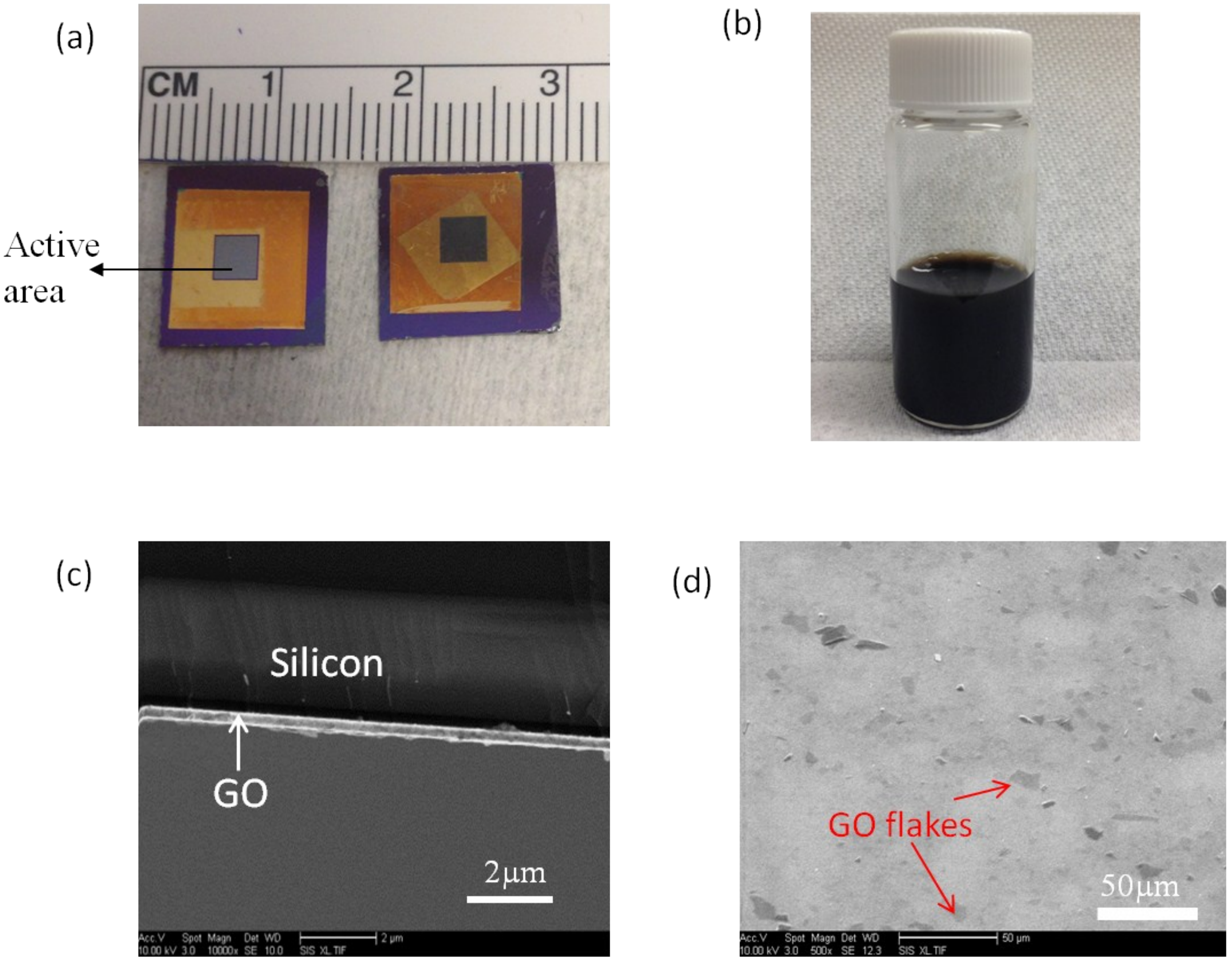

Figure S1. (a) Optical image of pristine Gr/Si solar Cell (left) and GO coated Gr/Si solar cell(right). Note that after GO coating, the color of the active area of device changed from grey to dark-blue, indicating a good ARC effect of GO coating. (b) Prepared 1mg/mL GO solution. (c) Cross-sectional SEM image, showing a uniform GO coating on Gr/Si solar. (d) Top-view SEM image of Gr/Si solar cell after GO coating.

3. Figure S2

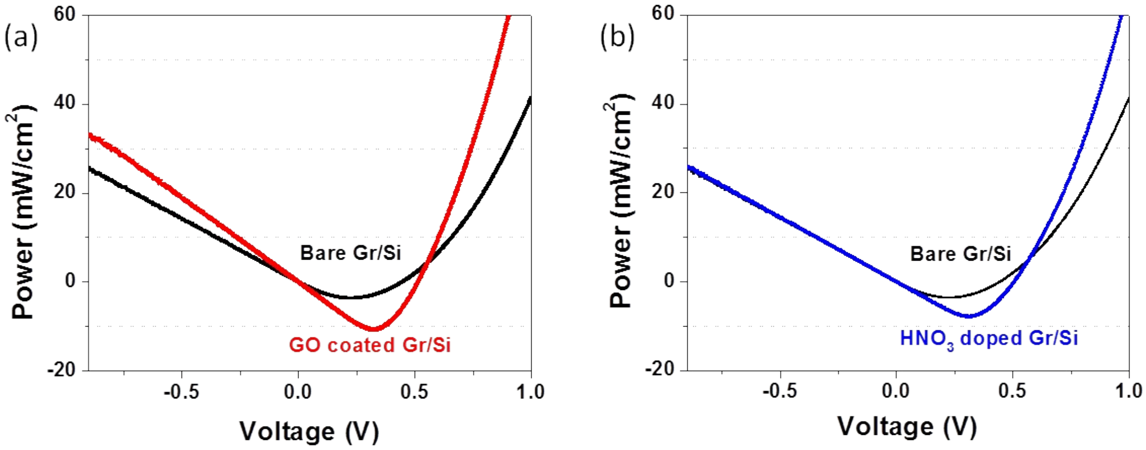

Figure S2. Power conversion efficiency (PCE) curves. (a) GO coated Gr/Si solar cell. (b) HNO_3 doped Gr/Si solar cell.

4. Figure S3

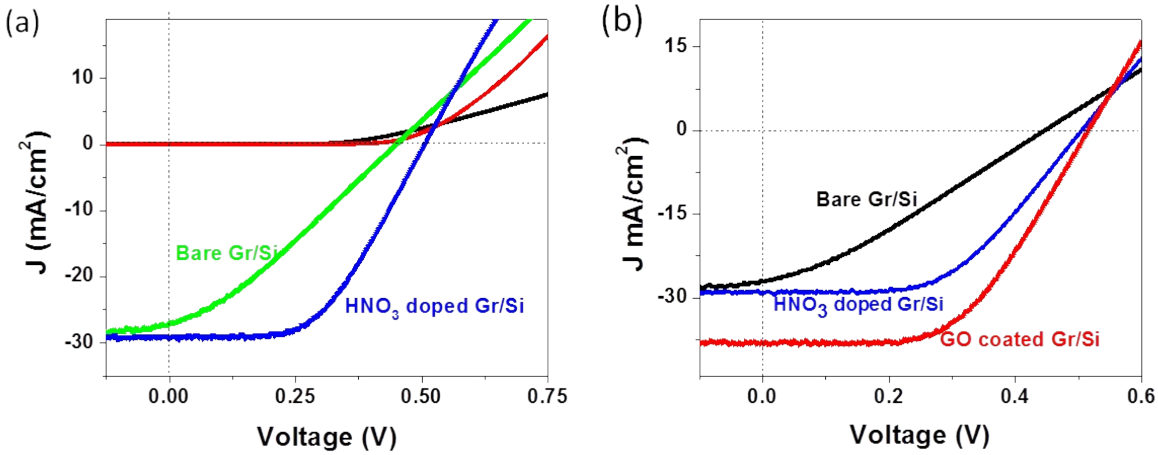

Figure S3. (a) *J-V* characteristic of pristine and nitric acid doped Gr/Si solar cell with light and without illumination. Black and red lines represent bare Gr/Si and HNO_3 doped Gr/Si solar cell, respectively, without illumination. (b) *J-V* characteristics of pristine (black), HNO_3 doped (blue), and GO coated (red) Gr/Si samples under standard illumination.

5. Figure S4

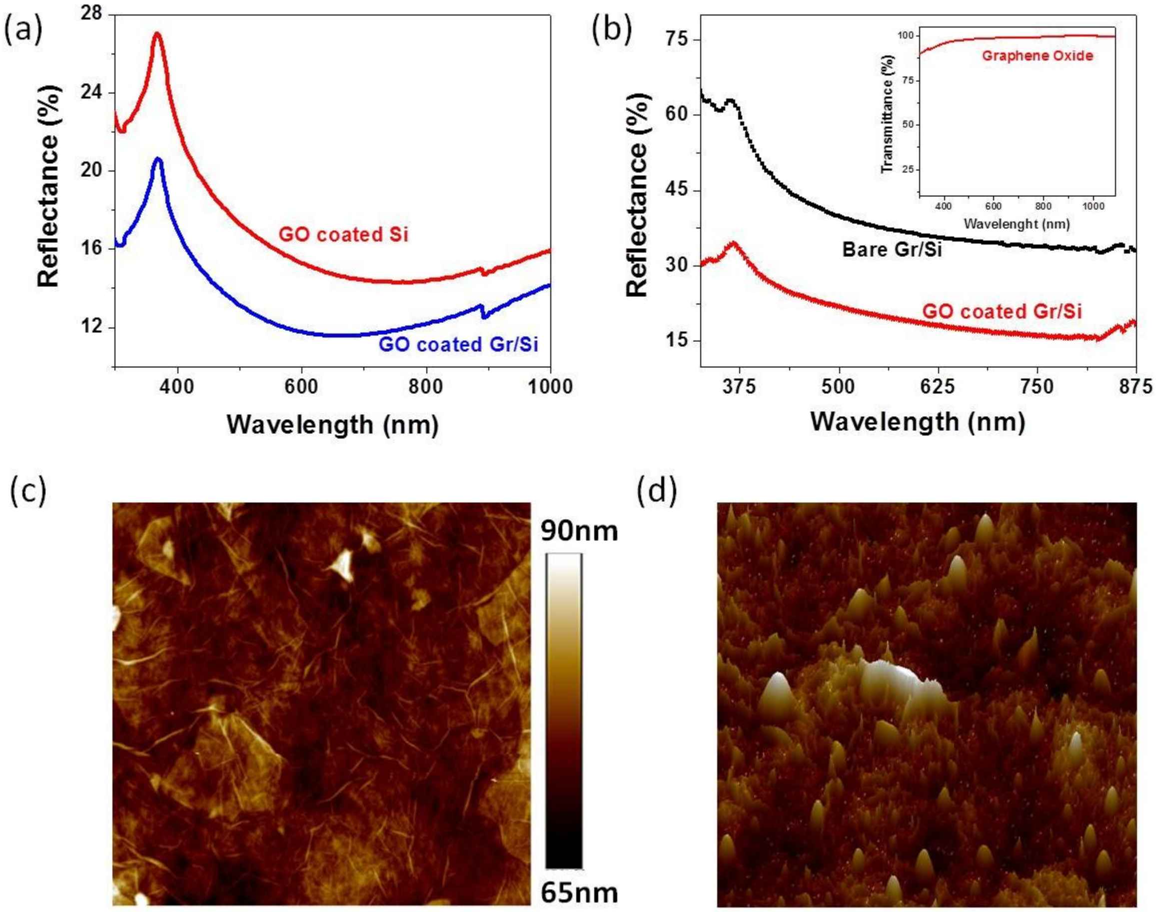

Figure S4. (a) Reflectance spectra of GO coated Si and GO coated Gr/Si samples showing the lower reflectance wavelengths. (b) Specular reflectance measurements of bare Si/Gr solar cell (black) and GO coated Gr/Si sample (red). Inset figure is transmittance of GO layer coated on glass. (c) and (d) are 2D and 3D AFM image of GO coated Gr/Si solar cell, respectively.

6. Figure S5

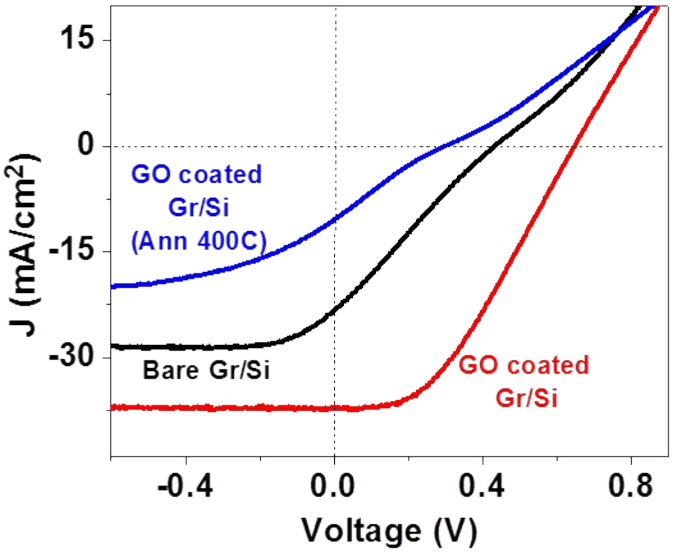

Figure S5. *J-V* characteristic of bare (black), GO coated Gr/Si solar cell before (red) and after annealing at 400°C (blue). It is clear that thermal annealing significantly reduces the V_{oc}, J_{sc} and *FF*, resulting in much lower efficiency, compare to the use of GO in the as-synthesized state.

7. Figure S6

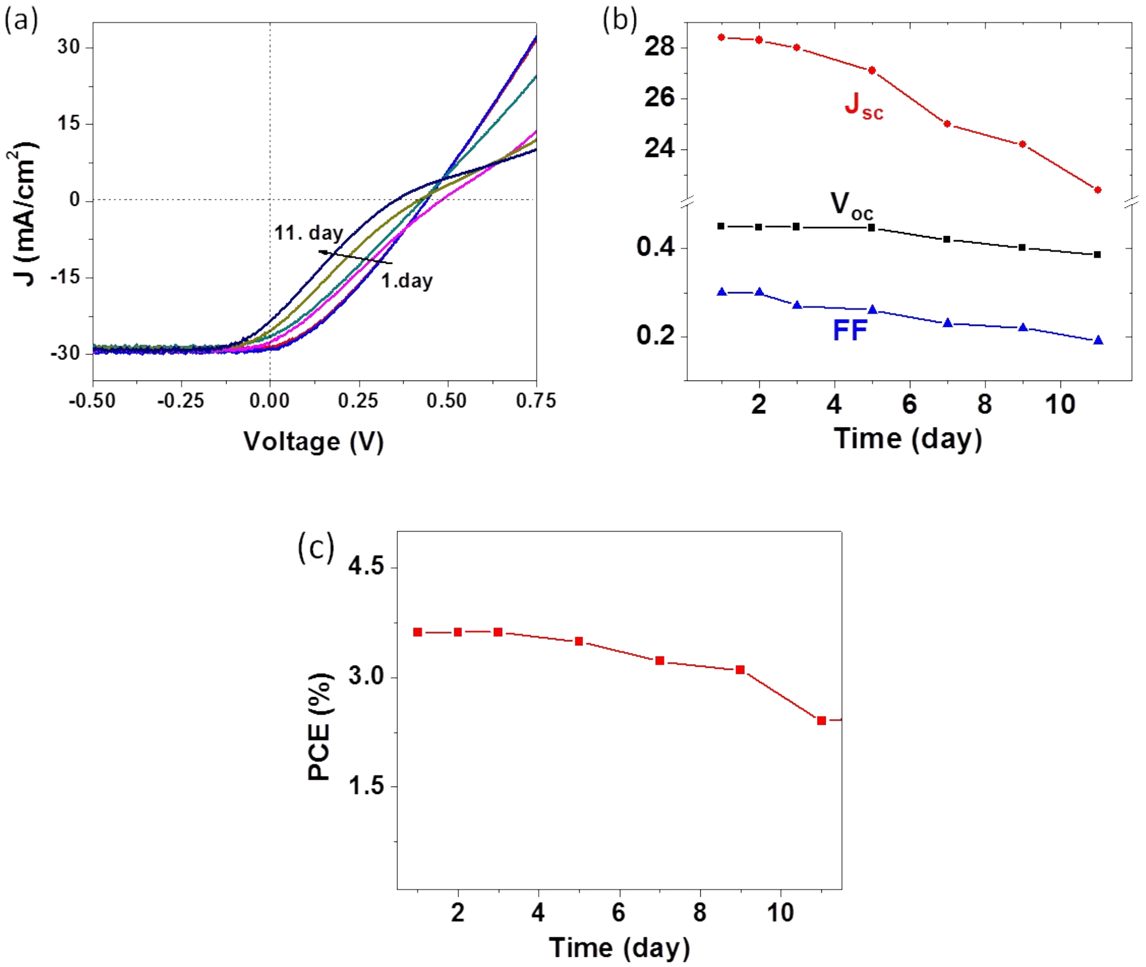

Figure S6. Stability of bare Gr/Si solar cell. (a) J-V characteristic of device from the 1st day to 11th day. As previously discussed in literature, forming of natural oxide layer causes a kink in *J-V* curve resulting in a poor FF after several days.[2] (b) Corresponding J_{sc}, V_{oc} and *FF vs.* time plot of bare Gr/Si solar cell. (c) PCE vs time plot of bare Gr/Si solar cell.

References:

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2. Song, Y.; Li, X.; Mackin, C.; Zhang, X.; Fang, W.; Palacios, T.; Zhu, H.; Kong, J. *Nano Lett.* **2015**, 15, 2104-2110.

3. Marcano, D. C.; Kosynkin, D. V.; Berlin, J. M.; Sinitskii, A.; Sun, Z.; Slesarev, A.; Alemany, L.B.; Lu, W.; Tour, J. M. *ACS Nano*, **2010**, 4, 4806-4814