Supporting Information

Large-Area, Transparent and Flexible Infrared Photodetector Fabricated Using P-N Junctions Formed by N-doping CVD-Grown Graphene

Nan Liu;[1] *He Tian;*[2,3] *Gregor Schwartz;*[1] *Jeffrey B.-H. Tok;*[1] *Tian-Ling Ren;*[2,3 *] *Zhenan Bao*[1*]

[1]Department of Chemical Engineering, Stanford University, Stanford, California 94305, USA

[2]Institute of Microelectronics, Tsinghua University, Beijing 100084, China.

[3]Tsinghua National Laboratory for Information Science and Technology (TNList), Tsinghua University, Beijing 100084, China

E-mail: RenTL@tsinghua.edu.cn; zbao@stanford.edu

Methods

Graphene synthesis and transfer. Large-area monolayer graphene was synthesized on Cu foils (99.98%, 0.025 mm thick, Alfa Aesar 13382) by low-temperature CVD. Prior to growth, the Cu foil was annealed at 160 mTorr in 10 sccm H_2 while temperature was raised to 1040 ^oC at 34 $^oC/min$ and maintained for 10 min. Growth was initiated by introduction of 30 sccm CH_4 and maintained for 30 min (pressure = 500 mTorr). The system was then cooled down to room temperature at 25 $^oC/min$ in 10 sccm H_2 and 30 sccm CH_4 (pressure = 500 mTorr).

To transfer the graphene onto target substrates, PMMA (M_w ~996, 000, Sigma-Aldrich 182265) was dissolved in chlorobenzene at 46 mg/ml and spin-coated on the graphene/Cu surface at 2000 rpm for 1 min. The PMMA/graphene/Cu stack was then heated at 100 ^oC for 10 min to remove the solvent. The un-protected graphene on the back side of the Cu foil was etched by O_2 plasma (150 sccm O_2, 150 W, 1 min). Cu was then removed by soaking the sample in 0.1 M ammonium persulfate [$(NH4)_2S_2O_8$, Sigma-Aldrich] for 2-3 hours. The PMMA/graphene stack was thoroughly rinsed in DI water and scooped onto target substrates (BCB-coated Si/SiO_2 or plastic). Lastly, PMMA was removed by soaking in acetone for 15 min and the sample was rinsed with isopropanol and DI water.

Device fabrication on rigid substrates. Using PMMA as carrier, the CVD grown graphene was transferred onto a SiO_2/Si substrate, which capped with a 20 nm thermally cross-linked divinyltetramethyldisiloxane bis(benzocyclobutene) (BCB) layer. Au electrodes were patterned by photolithography (channel length: 50 μm; channel width: ~1 cm). To control the area ratio of P- and N- region, another aligned photolithography step was applied with the Au patterns as markers. This second lithography step rendered regions in the resist layer for subsequently deposition of *o*-MeO-DMBI-I^- film (N-type dopants) in the thermal evaporation chamber. Therefore, certain regions of the channel are covered with *o*-MeO-DMBI-I^- film showing N-type behavior, while the unexposed regions contained the undoped transferred CVD graphene showing P-type behavior.

Optical and electrical characterization. To confirm the formation of P-N junctions, both Raman spectra and electrical transport measurements were performed. All Raman spectra were taken using a WiTech confocal Raman microscope, which is equipped with a piezo scanner and intensity-tunable 532 nm NiYAG laser. Using highly doped Si as a back gate, the three terminal transistor was measured using a Keithley 4200 semiconductor parameter analyzer in a N_2-filled glovebox. For the P-N junction devices, the transfer curves can be separated into three regions on the basis of two CNPs, which are p^+-p, p-n and n-n^+.

Photoresponse test. The photoresponsivity measurement was also performed using Keithley 4200 semiconductor parameter analyzer in a N_2-filled glovebox. IR irradiation, which was from solar simulator filtered to allow wavelength of >780 nm with an intensity of 45.65 mW/cm^2 to go through, was illuminated through a quartz window onto the entire device. To ensure that the measurement approach is consistent, we welded electrical wires to connect the electrodes and source measure units (SMU) on the Keithley 4200. To enhance the photoresponse of the photodetectors, a wide channel that is ~1 cm in width and 50 μm in length was designed. In-situ temperature changes were also recorded through a thermocouple that was in direct contact with the surface of device.

Transparent and flexible photodetector fabrication. The transparent photodetector is fabricated on a flexible polyethylene terephthalate (PET) substrate with ITO as electrodes. ITO was first deposited onto PET substrates and etched into the designated electrode patterns using photolithography. Subsequently, CVD-grown graphene was transferred onto this pre-patterned ITO-PET substrate to form a top contact with ITO, and then spatially N-type doped to form P-N junction as described above. The detailed fabrication process was illustrated in **Figure S8**. PET, together with commonly used substrates such as polyimide (PI), polyethylene naphthalate (PEN) and glass, are all compatible with this fabrication process.

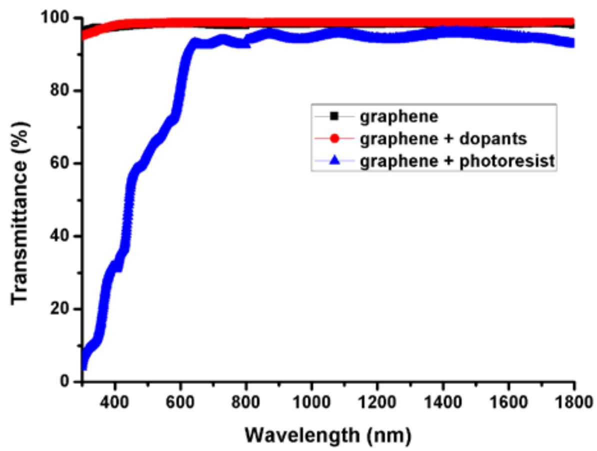

Figure S1 UV-vis-IR transmittance spectra of undoped, N-doped (3 nm *o*-MeO-DMBI-I⁻ film) and photoresist (S1813, 5000rpm, 45s) covered CVD-grown graphene.

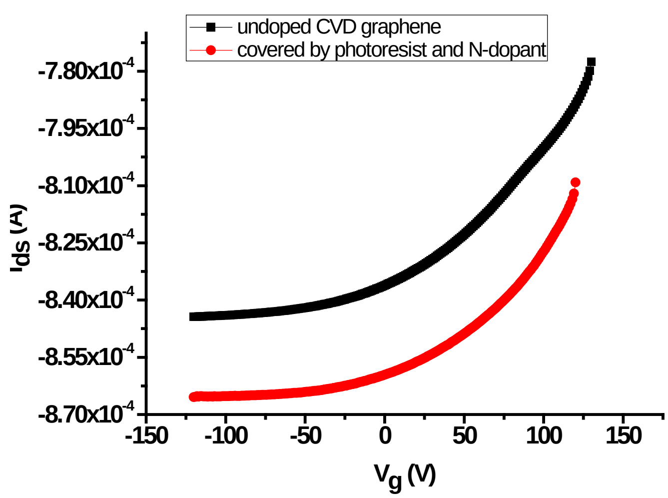

Figure S2 Transfer curves of undoped transferred CVD graphene before (black) and after (red) covering a layer of photoresist (S1813, 5000rpm, 45s) and 2 nm *o*-MeO-DMBI-I⁻ film. This illustrates that undoped transferred graphene is highly P-type, and covering a layer of photoresist can efficiently protect the P-type region against N-type dopants, maintaining its P-type behavior.

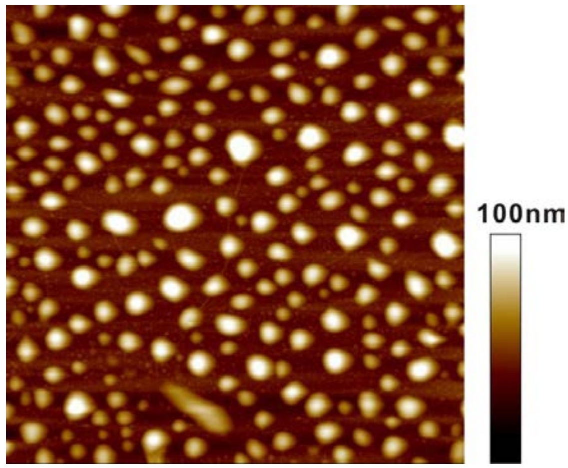

Figure S3 AFM image of transferred CVD graphene which was covered by 3 nm *o*-MeO-DMBI-I^- film on BCB/SiO_2/Si substrate.

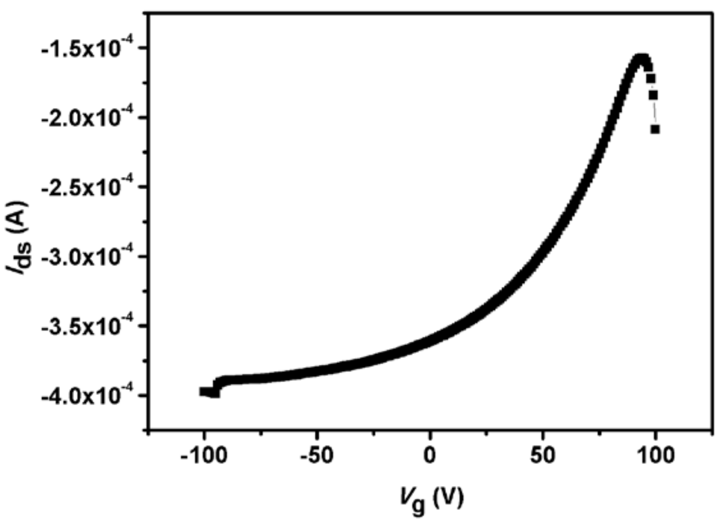

Figure S4 Transfer curve of p-type graphene device (channel width: 10 μm; length: 5 μm, V_{ds} = 0.1 V).

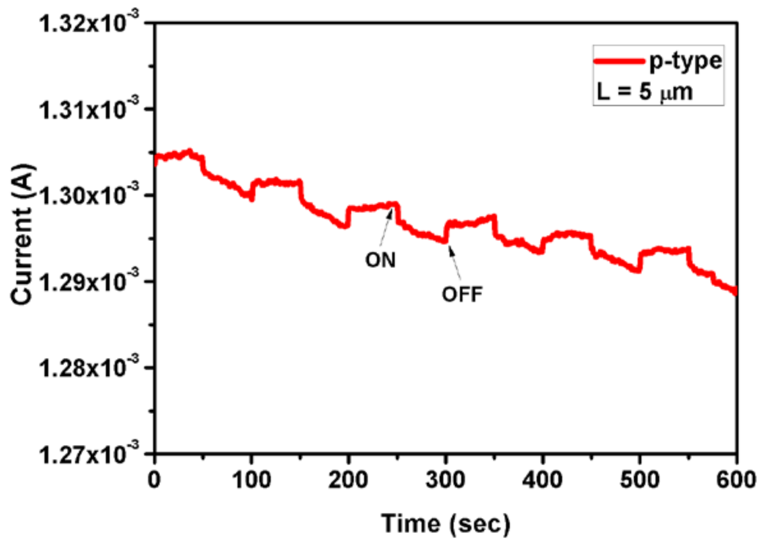

Figure S5 Photoresponse of short-channel p-type graphene photodetector, showing a negative photoresponse under IR illumination (> 780 nm).

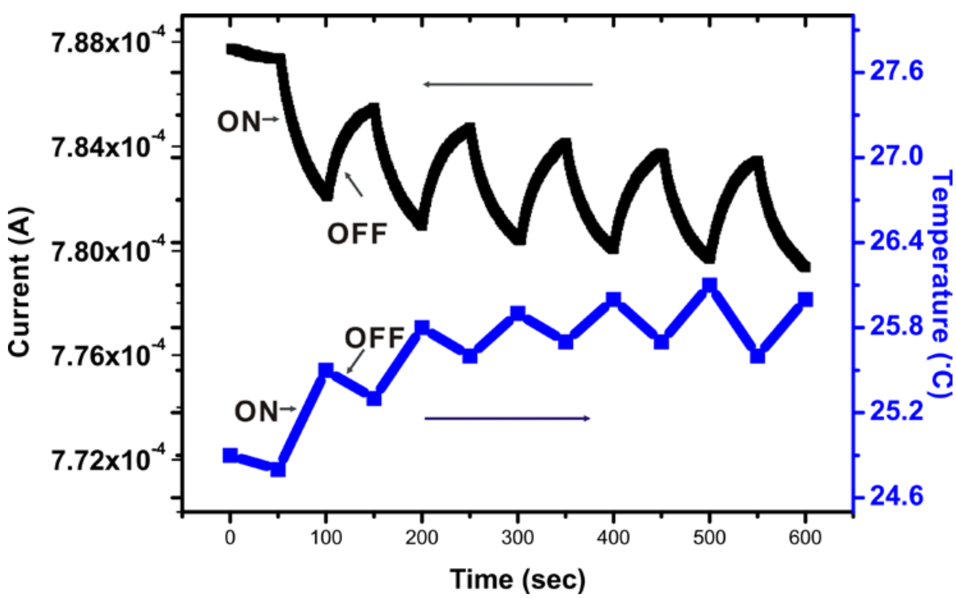

Figure S6 Representative photoresponse of long-channel P-N junction graphene photodetector under IR illumination (>780 nm) and their corresponding changes in the temperature (shown in blue dotted lines).

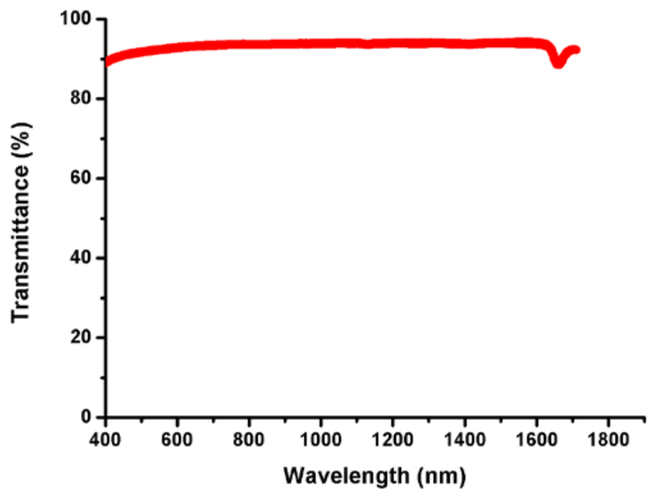

Figure S7 UV-vis-IR transmittance spectrum of a P-N junction graphene photodetector, showing that the transmittance is >~90% over a wavelength range of 400 - 800 nm and >93% in the IR range of 800 - 2000 nm.

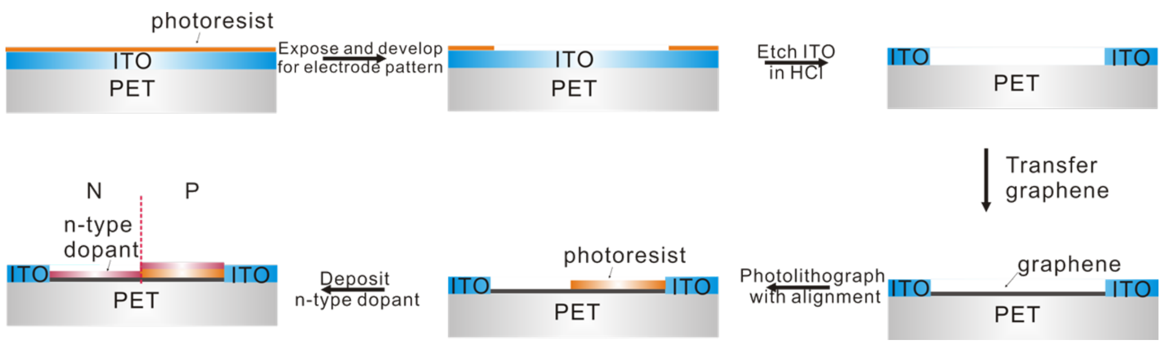

Figure S8 Schematic showing the process of chemically doping CVD-grown graphene on PET substrates into P-N junctions. ITO works as transparent electrodes here. CNTs, PEDOT and other commonly used transparent electrodes can also be compatible with this fabrication process.

Table S1 Comparison of photoresponse of our device with literature. Photocurrent vs. dark current ratio has been normalized by illumination power.

Source	Device structure	Measured condition	Photocurrent vs. dark current (%)	Response time
Nature Photonics, 2013, 7, 53	Biased homogeneous graphene	Laser (690 nm, 96.19mW/cm^2) $V_g = \pm 5V$, 296 K	~ 0.07%	<1 s
Nature Communications, 2013, 4, 1811	Etched graphene	Laser (532 nm, 633 mW/cm^2)	~0.02 % (294 K); 0.9% (12 K)	>1 s
Advanced Materials, 2011, 23, 5419	Reduced graphene oxide (RGO); Graphene nanoribbons (GNR)	Laser diode (1550 nm, 80 mW/cm^2) 296 K	-13% (RGO)[†] -11.4% (GNR)[†]	2 s (RGO) 87 s (GNR)
This work	Chemically doped P-N junction	Global IR (> 780 nm, 45.65 mW/cm^2), 298 K	~ 5.0%	<1 s

[†]Set dark current direction as positive