

## Supporting Information

### Reversible Photochemical Control of Doping Levels in Supported Graphene

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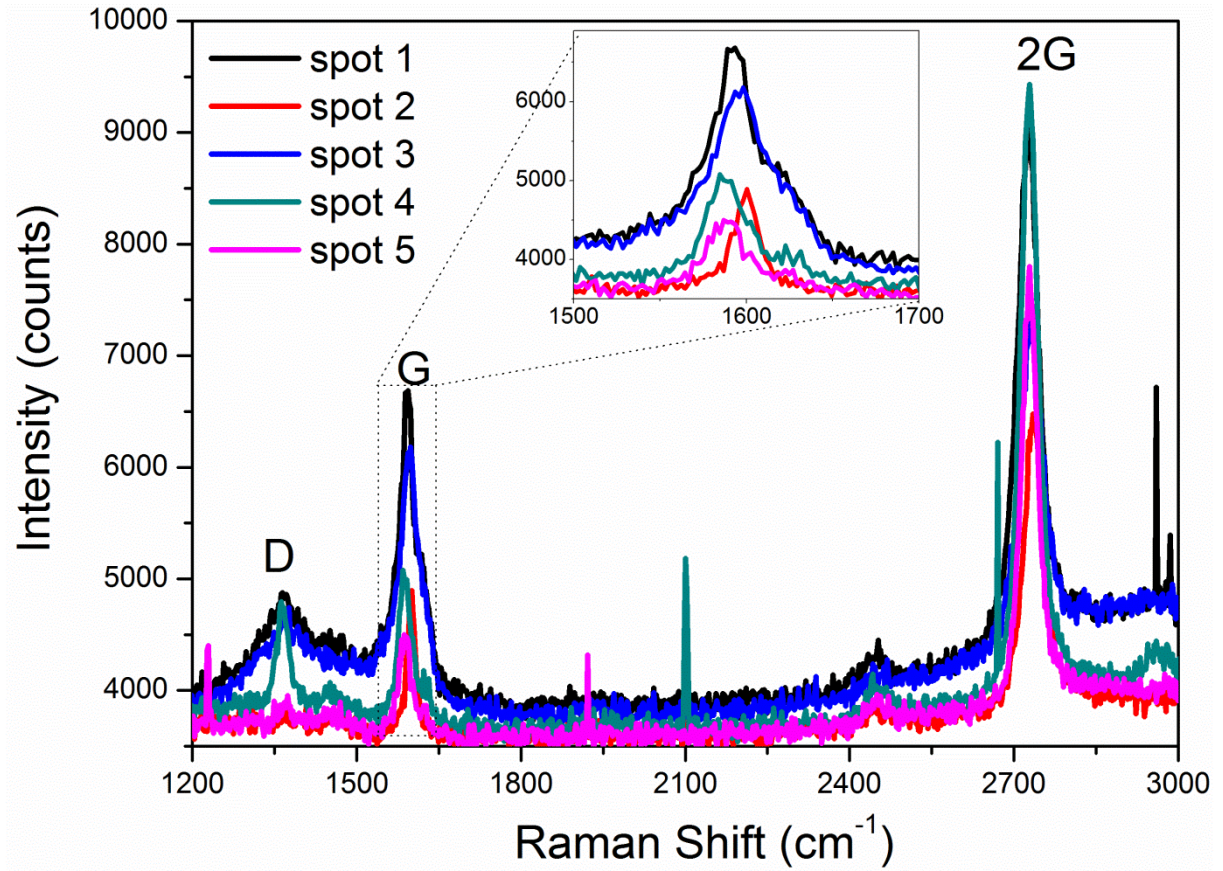
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## **Content**

- 1. Raman characterizations*
- 2. Doping stability and reversibility test at different atmosphere*
- 3. Doping reversibility test*
- 4. Photochemical doping effects: 800nm vs 400nm*
- 5. THz time domain spectroscopy characterizations*
- 6. Pure N<sub>2</sub> purging effect on the graphene resistance*
- 7. Pure N<sub>2</sub> purging or vacuum effect on THz photoconductivity*
- 8. Graphene mobility estimation before/after photochemical treatment*

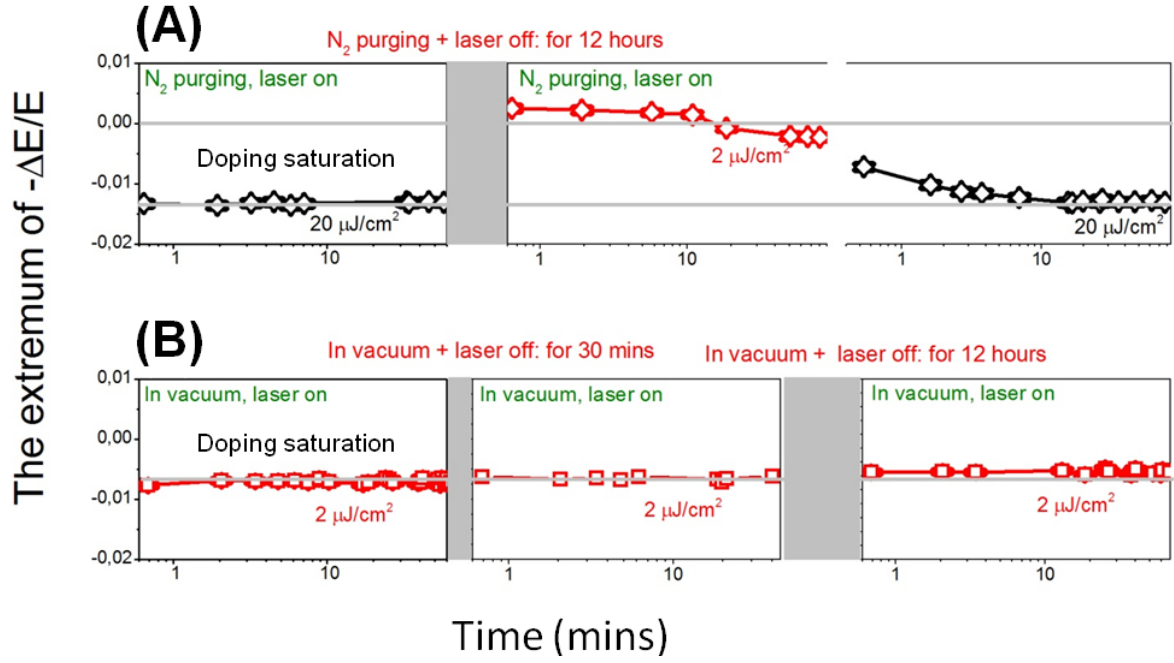
## 1. Raman characterizations



**Figure S1.** Raman spectra for five different spots of an N-doped sample in our study (sample F). The inset shows the zoomed-in G-band Raman spectra.

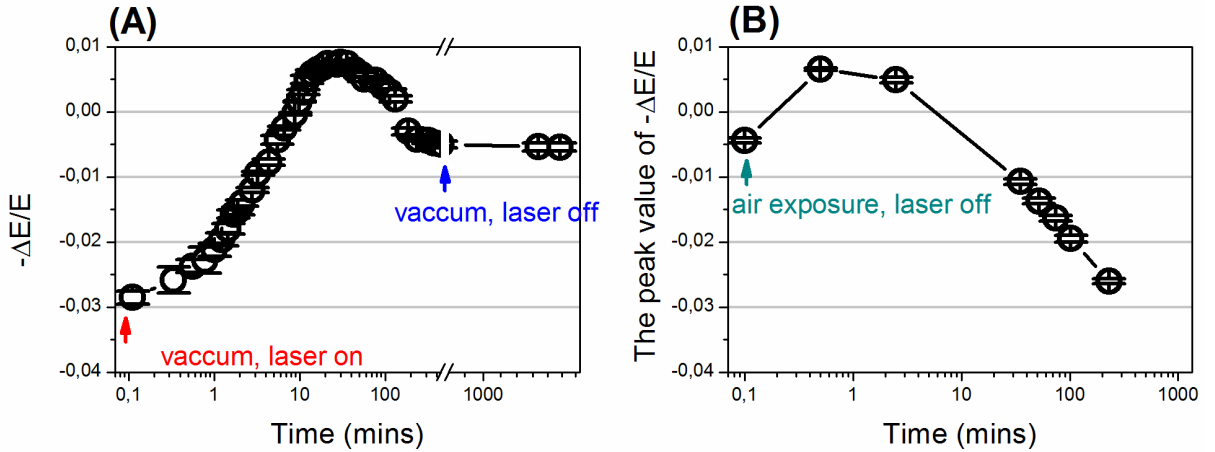
## 2. Doping stability test in $N_2$ purging or vacuum atmosphere

While the photoinduced THz conductivity change is completely reversible by terminating optical treatment and exposing doped graphene to air ( $O_2$  concentration 20.8%), we find the effect is partially reversible in  $N_2$  purging condition ( $O_2$  concentration  $4.5 \pm 0.3\%$ ), and completely stable in vacuum for over 12 hours.



**Figure S2.** Doping stability test in (A)  $N_2$  purging (sample F) with 4.5%  $O_2$  partial pressure and (B) vacuum conditions (sample G).

### 3. Doping reversibility test

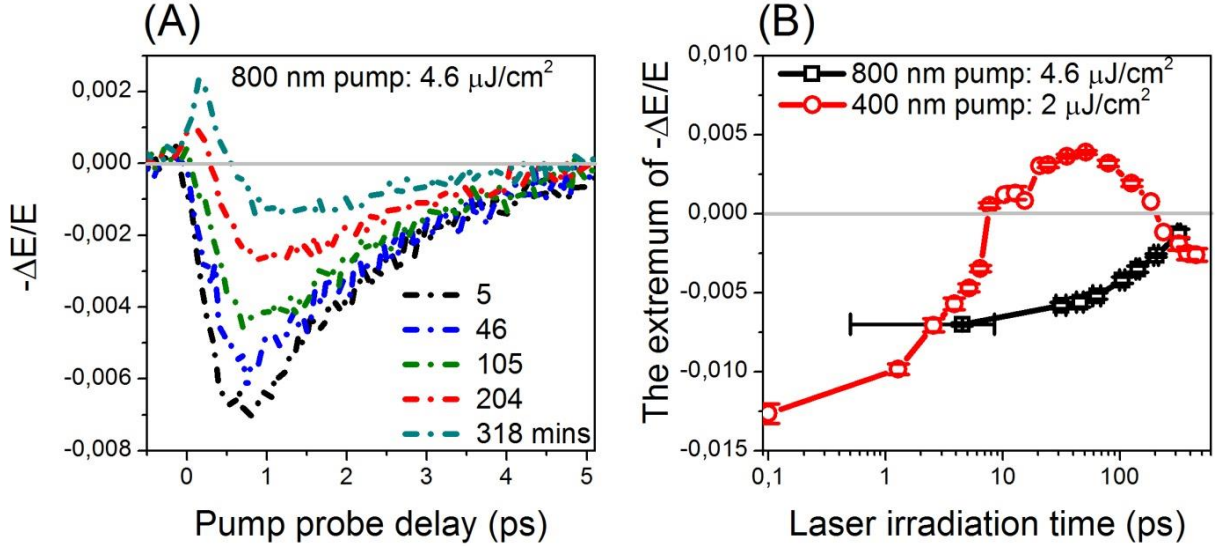


**Figure S3.** (A) Photochemical doping effect in graphene (based on sample C); (B) Doping reversibility test after sample exposing to air while terminating laser.

Photochemical treatments based on sample C is conducted in vacuum. After that, the chamber is open to air and the laser is blocked. At a given time of interest, THz conductivity is used to monitor the doping level in the graphene. By a similar approach discussed in the text (measurements for Figure 1(D)), for minimizing the optical excitation effect during measurements, we only monitor the

maximum change of the photoconductivity peak value within a short laser excitation less than 10 seconds for a given time of interest. The results are shown in Figure S3(B).

#### 4. Photochemical doping effects: 800nm vs 400nm



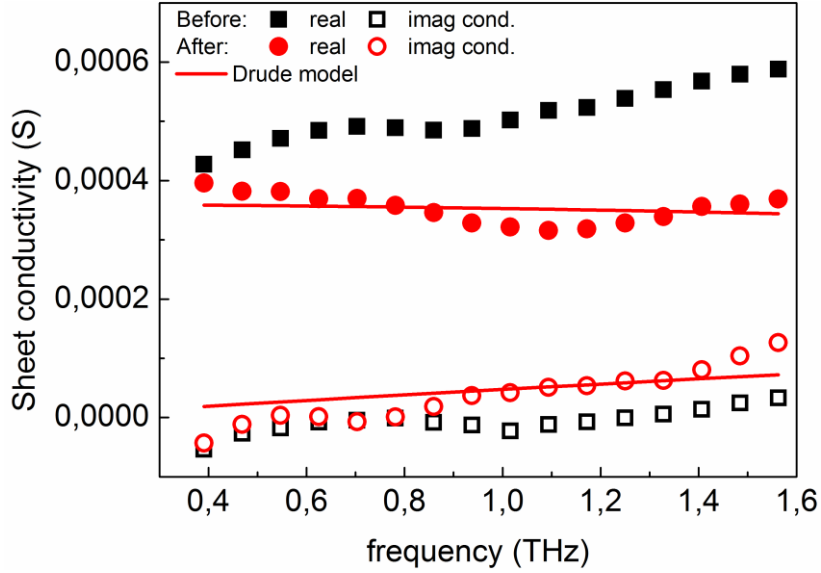
**Figure S4.** The photochemical doping effect by 800 nm laser irradiation treatment (sample A). (A) The OPTP carrier dynamics evolution in graphene as a function of 800 nm pulsed laser irradiation treatment time, with a fixed fluence of  $4.6 \mu\text{J}/\text{cm}^2$ ; (B) The peak magnitude of the photo-induced THz change ( $-\Delta E/E \sim 0.5$  ps after the excitation pulse) over time under 800 nm laser irradiation treatment, and its comparison to 400 nm treatments.

#### 5. THz time domain spectroscopy characterizations

We use terahertz time domain spectroscopy to measure the AC conductivity of graphene in the THz range 0.4–1.6 THz. In this measurement the optical transmittance of the sample is measured in the THz range; THz waveforms transmitted through the graphene sample (denoted  $E(t)$ ) and waveforms transmitted through a bare substrate (denoted  $E_0(t)$ ) are recorded. Based on Fourier transformation, the complex sheet conductivity of the graphene sample can be calculated by:

$$\frac{E(\omega)}{E_0(\omega)} = \frac{n+1}{n+1+\sigma(\omega)Z_0} \quad \text{Equation (S1)}$$

Where  $n = 1.95$  is the THz refractive index of the substrate and  $Z_0 = 376.63 \Omega$  the impedance of vacuum.



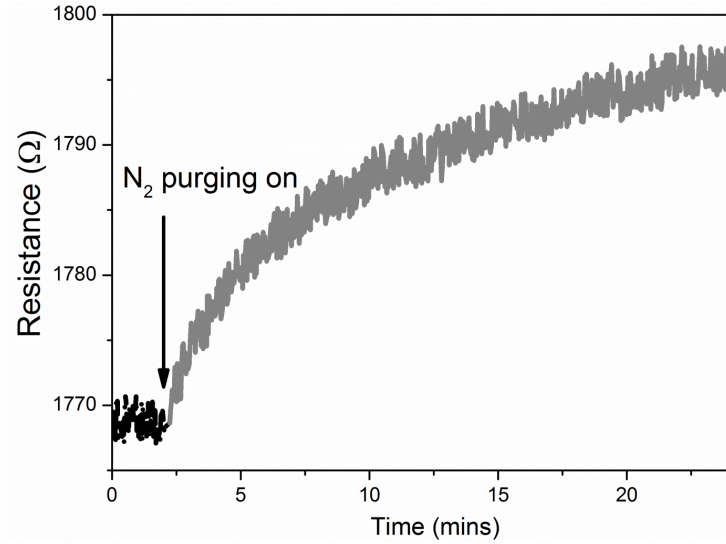
**Figure S5.** The measured THz conductivity of graphene before (black symbols) and after (red symbols) photo-gating. The real part of the conductivity is shown by the full symbols; the empty symbols represent the imaginary part. The solid lines show the fit by the free carrier (Drude) model.

The results of the measurements are displayed in Figure S5 for our graphene sample both before and after photo-doping. The conductivity originates from the free motion of carriers in the bandgap and therefore it can be fitted by the Drude model for graphene:

$$\sigma(\omega) = \frac{e_0^2}{\pi \hbar^2} |E_F| \frac{\tau}{1 - i\omega\tau} \quad \text{Equation (S2)}$$

Where  $e_0$  is the elementary charge,  $\hbar$  the reduced Planck constant,  $E_f$  the Fermi-level and  $\tau$  the carrier scattering time. From the fit (see the red solid lines in Figure S5) we obtain the values  $\tau = 20 \pm 10$  fs and  $E_f = 150 \pm 75$  meV.

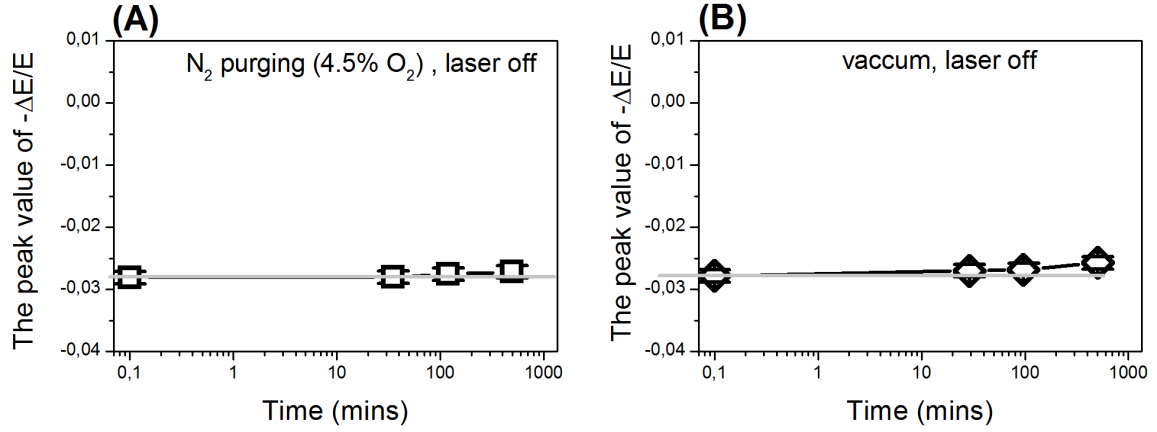
## 6. Pure $N_2$ purging effect on the graphene resistance



**Figure S6.** Pure  $N_2$  purging effect on graphene resistance (sample H). The 2-point resistance change in a graphene sample without laser pulse illumination treatments is monitored before/after starting  $N_2$  purging.

As discussed in the main text, we have shown that under 400 nm laser pulse illumination treatment and a  $N_2$  purging condition, a change of the two-point resistance of  $>7000 \Omega$  in graphene devices has been observed. In order to separate the contribution of  $N_2$  purging from laser illumination treatment, a two-point resistance change in the dark has been monitored over time with only  $N_2$  purging. As shown in Figure S6, the resistance of graphene in air without laser illumination is constant over time. Upon  $N_2$  purging, we observe a small increase ( $\sim 25 \text{ Ohm}$ ) and a gradual saturation of resistance within 30 mins. This change is negligible compared to the resistance change induced by laser illumination treatment.

## 7. Pure $N_2$ purging or vacuum effect on THz photoconductivity



**Figure S7.** (A) Pure N<sub>2</sub> purging, (B) vacuum effect on graphene THz photoconductivity (based on sample C).

### 8. Graphene mobility estimation before/after photochemical treatment

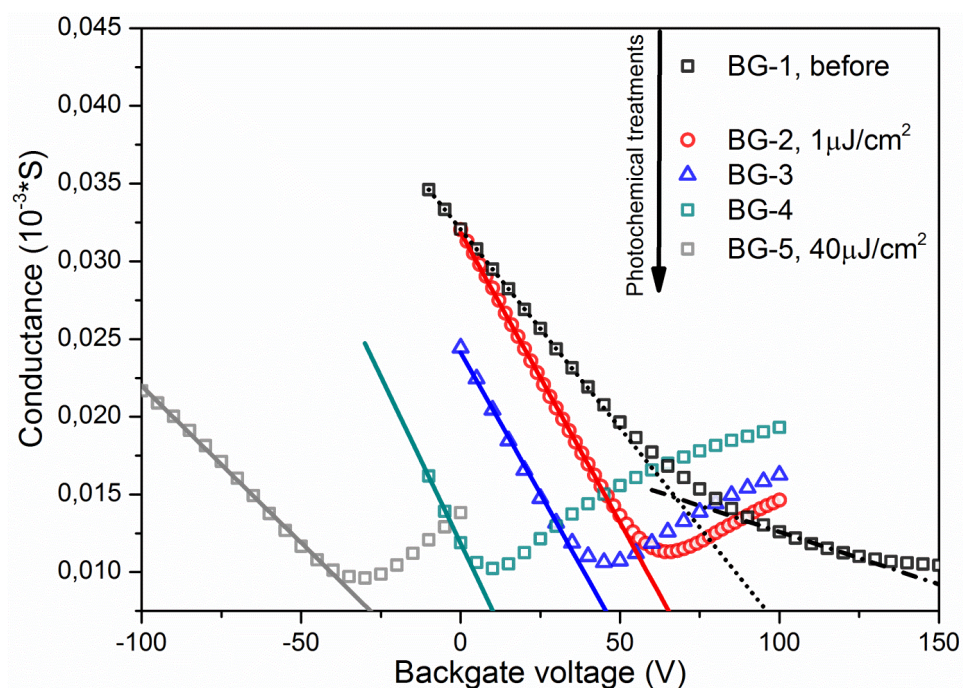
The model used for mobility estimations in our devices before/after photochemical treatments has been reported in previous studies in ref. 46 in the main text. This method assumes the sample to be a simple capacitor with SiO<sub>2</sub> as a dielectric:

$$\frac{1}{R} = \sigma = \mu * c_g * (V_g - V_{g, \min}) \quad \text{Equation (S3)}$$

In which,  $R$  is the 2-point resistance of the sample,  $V_{g, \min}$  is the gate voltage at Dirac point, and  $c_g$ ,  $\sigma$ ,  $\mu$ ,  $V_g$  are the capacitance of SiO<sub>2</sub>, conductivity, mobility of the sample and backgate voltage respectively. Around the value  $V_{g, \min}$  the conductance can be assumed to be linear (i.e. the mobility is constant) and fitted with a straight line (with a slope of  $\mu * c_g$ ), as shown in Figure S7 the conductance of the sample before/after photochemical treatments. With the known gate capacitance of SiO<sub>2</sub>  $c_g = \epsilon \epsilon_0 / d = 1.15 \cdot 10^{-4} \text{ F/m}^2$  based on geometrical calculation, one can estimate the electron mobility  $\mu$  of the sample.

The accuracy of the mobility estimation for the BG-1 measurement (the initial state before any treatment) is compromised by the fact that we did not reach the Dirac point of the sample even at the backgate voltage as high as +150 V. We then estimated the 2 mobility limits in the sample as shown in Figure S8 (maximum by dotted line fitting and minimum by the dot-line fitting) as 6 and 14 cm<sup>2</sup>/V\*s.





**Figure S8.** Graphene mobility estimation before/after photochemical treatments in graphene (sample B). BG-1 is the back gate (BG) measurement before the photochemical treatment. From BG-2 to BG-5, the photochemical treatments are employed and the fluences are increased gradually from 1 to 20  $\mu\text{J}/\text{cm}^2$ .