# Mid-infrared gas sensing using graphene plasmons tuned by reversible chemical doping

(Supporting Information)

Nestor Jr. Bareza<sup>‡</sup>, Kavitha K. Gopalan<sup>‡</sup>, Rose Alani<sup>‡</sup>, Bruno Paulillo<sup>‡</sup>\*, and Valerio Pruneri<sup>‡#</sup>

<sup>‡</sup>ICFO-Institut de Ciencies Fotoniques, The Barcelona Institute of Science and Technology,

08860 Castelldefels, Barcelona, Spain

<sup>#</sup>ICREA-Institució Catalana de Recerca i Estudis Avançats, Passeig Lluís Companys, 23, 08010

Barcelona, Spain.

\*Corresponding e-mail: bruno.paulillo@icfo.eu

#### S1. Optical response of the as-prepared GNR surface

The spectral response of the GNR array was tested before PEI functionalization. The LSPR mode is dynamically tuned via electrostatic gating by applying a back-gate voltage V<sub>BG</sub> between +20V and -80V (Fig S1.a). For zero bias, we observe that the as-prepared GNR surface is slightly pdoped due to the fabrication process, with charge neutrality point (CNP) around V<sub>BG</sub> =+20 *V*. For higher negative V<sub>BG</sub> the LSPR mode blue-shifts and grows in strength due to the increased pdoping, as expected. Fig S1.b shows the simulated extinction spectra of a GNR array with the same geometry used in experiments. The graphene damping is set to  $\gamma = 6.7 \cdot 10^{13} \text{ s}^{-1}$  to reproduce the experimental LSPR linewidth and the Fermi energy (E<sub>F</sub>) is swept from 0.05 eV to 0.2 eV to compare with experiments. The intrinsic doping of the as-prepared GNR surface is estimated to be around E<sub>F</sub> = -0.15 eV.

The Fermi energy dependence as a function of V<sub>BG</sub> for the GNR surface as-prepared ( $V_{CNP} = +20V$ ) and with PEI coating ( $V_{CNP} = -80V$ , see main text) is depicted in Fig S1.c. This is calculated as<sup>1</sup>

$$|E_F| = \hbar v_F \sqrt{\pi \frac{C_{ox}}{q_e} |V_{CNP} - V_{BG}|}$$

where  $\hbar$ ,  $v_F$ ,  $q_e$  and  $C_{ox}$  are the reduced Planck constant, Fermi velocity (1.15x10<sup>8</sup> cm/s), fundamental electric charge and capacitance of the 285 nm-thick oxide ( $C_{ox} = \frac{\epsilon_0 \epsilon_{ox}}{t_{ox}}$ ,  $\epsilon_{ox} = 3.9$ SiO<sub>2</sub> permittivity), respectively.



Figure S1. (a) Plasmonic response of as-prepared GNR surface at different  $V_{BG}$  and (b) corresponding simulations for different graphene Fermi levels. (c) Fermi energy versus  $V_{BG}$  of as-prepared and PEI-coated GNR surface.

## S2. PEI-CO2 vibrational fingerprints

The interaction of PEI with CO<sub>2</sub> gas occurs via zwitterion mechanism, wherein the basic amine groups of PEI polymer react covalently with the hard-acidic CO<sub>2</sub> molecules even under atmospheric thermal condition<sup>2</sup>. Interaction of CO<sub>2</sub> with primary (RNH<sub>2</sub>) and secondary (R<sub>2</sub>NH) amines forms carbamate (R<sub>2</sub>NCOO<sup>-</sup>) compounds following reversible chemical reactions as illustrated in Ref [2] (R represents species from alkyl group). The reversibility in regenerating amines can be done by thermal desorption of CO<sub>2</sub> with 85°C heat treatment or above<sup>3</sup>. Moreover, CO<sub>2</sub> interacting with tertiary amines which results in the production of bicarbonates (HCO<sub>3</sub><sup>-</sup>) under humid conditions<sup>4</sup>. The chemical compounds resulting from PEI-CO<sub>2</sub> interaction have natural midinfrared (MIR) frequency vibrations as summarized in Table S2.

Frequency (cm <sup>-1</sup> )	Assignment	
1101	C=O symmetric stretch in R <sub>2</sub> NCOO-	
1304	Conformational change in $HCO_3^-$	
1380	Asymmetric stretch in carbonate	
1475, 1488	NCOO skeletal vibration	
1550, 1565	$C=0$ asymmetric stretch in $R_2NCOO^{-1}$	
1636, 1650	N-H deformation in $NH_3^+$	
3055	N-H stretch in $NH_3^+$	
3360	Asymmetric NH <sub>2</sub> stretch	
3420, 3439	N-H stretch in RN-HCOO <sup>-</sup>	

Table S2. Frequency assignments of product species from PEI-CO<sub>2</sub> interaction<sup>5-9</sup>.

#### S3. Ultrathin PEI film characterizations

Two solutions are prepared with branched PEI diluted in ethanol, having 0.76 wt% and 0.22 wt% concentrations. The thicknesses of spin-coated PEI films on silicon are 30 nm and 9 nm, respectively, which are evaluated from ellipsometric fitting (Fig S3.a). Surface morphologies imaged with AFM (Figs S3.b and S3.c) depict continuous films, with both having RMS roughness around 0.3 nm.

Ultrathin polymer film has several advantages compared to its bulk counterpart. For one, this avoids the optical loss contribution due to interference in thick polymers. Also, it allows shorter path length for gas species, thus yielding faster response due to easier diffusion and faster thermal desorption processes. Fig S3.d displays the spectral changes of two PEI films when thermally desorbed at 100°C for 2 mins in ambient air. Three prominent peaks at 1304, 1475 and 1565 cm<sup>-1</sup> correspond to  $HCO_3^-$  vibration, NCOO skeletal vibration and C=O stretch, respectively. The peaks

are more pronounced with 30 nm film as expected with larger interaction length. Flatter spectral response is observed with 9 nm film when heated, indicating easier CO<sub>2</sub> desorption from the film.



Figure S3. (a) Ellipsometry parameters ( $\alpha$ ,  $\beta$ ) fitting of spin-coated PEI layer from two solutions of 0.76 wt% and 0.22 wt% in ethanol, yielding 30 nm and 9 nm ultrathin films, respectively. Surface morphologies of (b) 30nm and (c) 9nm PEI membranes are imaged with atomic force microscopy (AFM), both having approximate RMS roughness R<sub>q</sub>~0.3 nm. (d) Extinction spectra comparing thermal desorption at 100°C of PEI between 9 and 30 nm films on CaF<sub>2</sub>.

#### S4. PEI permittivity model

To derive the complex permittivity of the ultrathin PEI film of Fig.2d, we used the Lorentz model with 5 oscillators corresponding to the visible PEI vibrational bands in the spectral range 1200-1800 cm<sup>-1</sup>. The multi-Lorentz relative permittivity is written as:

$$\varepsilon_{PEI} = \varepsilon_{\infty} + \sum_{j=1}^{5} \frac{S_j}{1 - \left(\frac{k}{k_{0j}}\right)^2 - i\gamma_j \left(\frac{k}{k_{0j}}\right)}$$

where  $\varepsilon_{\infty} = 2.56$  is obtained via ellipsometry characterization and the remaining parameters are optimized by fitting the transmission *T* data of a 9 nm PEI film on an IR-transparent substrate (CaF<sub>2</sub>). To this end, a fitting code was written in Python using the TMM package by S. Byrnes<sup>10</sup>. The experimental and fitted *T* spectra are shown in Fig. S4 and the fitting parameters in Table S4.



Figure S4. Experimental vs fitted T spectrum for 9 nm PEI film on CaF<sub>2</sub>

Table S4. Extracted fit parameters for multi-Lorentz PEI permittivity model

	$k_{\theta j} ({ m cm}^{-1})$	$S_j$	Yj
1	1300	0.012	0.05
2	1404	0.005	0.04
3	1474	0.013	0.04
4	1560	0.019	0.04
5	1700	0.005	0.06

#### S5. CO2 sensing with bare GNR

Figure S5 illustrates the control experiment of CO<sub>2</sub> sensing using GNR without ultrathin PEI film. No significant change is observed in the spectral response for varying CO<sub>2</sub> concentrations, varied with similar ppm range in the test experiments. When combined with ultrathin PEI film (Figure 3a, main text), the plasmonic response is tuned for various concentration levels. This supports the hypothesis that the tunable effect mainly arises from chemical doping of GNR associated to a change of PEI, this change being proportional to the gas concentration.



Figure S5. Extinction spectra of GNRA (width w=45nm and period p=80nm) on SiO<sub>2</sub>/Si substrate exposed with different CO<sub>2</sub> ppm levels.

S6. Deconvolution of LSPR and PEI vibrational frequency peaks.

The deconvolution of PEI extinction spectrum shown in Fig S6.a is done using a 5-peak Lorentzian fitting function whose central positions can be referred to the vibrational frequencies summarized in Table S2. The extinction spectrum of GNR+PEI surface shows the coupling of the graphene LSPR resonance with the PEI vibrational modes, occurring as dips in the LSPR peak (Fig S6.b). The fitting function for the asymmetric LSPR line shape is taken from the paper of Ju et al.<sup>11</sup>.



Figure S6. Deconvolution fitting for the extinction spectrum of (a) PEI alone and (b) GNR+PEI.

## S7. Cyclic CO2 sensing of ultrathin PEI film

The response to CO<sub>2</sub> ppm variations of PEI film only is also recorded (Fig S7), alongside the three cycles of test measurements. The repeatability is confirmed for days 2 and 20, with PEI regeneration at 95°C for 1.5 min. Here, the sensing response can be monitored by intensity change of the peaks, whereas sensing with hybrid GNR-PEI can be quantified via plasmonic changes (variations in peak intensity and peak wavelength). An extra strong peak at 1684 cm<sup>-1</sup> is observed on day 20, this being likely related to urea formation<sup>12</sup>.



Figure S7. Cycle measurements of spectral evolution for different CO<sub>2</sub> ppm level exposures of PEI directly on SiO<sub>2</sub>/Si substrate.

### S8. GNR LSPR peak position versus Fermi energy

The dependence  $k_{LSPR}$  versus the  $E_F$  used in the main text to estimate the change in  $E_F$  upon CO<sub>2</sub> exposure has been derived from the simulations in the left panel of Fig.S8. The extinction spectra have been computed as described in Methods and  $E_F$  has been swept from 0.1 to 0.55 eV. The linear fit in the right panel of Fig.S8 yields  $\frac{\Delta k_{LSPR}}{\Delta E_F} = 1216 \ cm^{-1}/eV.$ 



Figure S8. (left) Simulated extinction spectra vs Fermi energy E<sub>F</sub> for the GNR surface of the study.

(right). LSPR peak position vs E<sub>F</sub>. The linear fit gives a slope of 1216 cm<sup>-1</sup>/eV.

#### REFERENCES

- Wang, F.; Zhang, Y.; Tian, C.; Girit, C.; Zettl, A.; Crommie, M.; Shen, Y. R. Gate-Variable
   Optical Transitions in Graphene. *Science* (80-. ). 2008. https://doi.org/10.1126/science.1152793.
- (2) Littel, R. J.; Versteeg, G. F.; Van Swaaij, W. P. M. Kinetics of CO2 with Primary and Secondary Amines in Aqueous Solutions-I. Zwitterion Deprotonation Kinetics for DEA and DIPA in Aqueous Blends of Alkanolamines. *Chem. Eng. Sci.* 1992. https://doi.org/10.1016/0009-2509(92)80319-8.
- (3) Drage, T. C.; Smith, K. M.; Arenillas, A.; Snape, C. E. Developing Strategies for the Regeneration of Polyethylenimine Based CO2 Adsorbents. In *Energy Procedia*; 2009. https://doi.org/10.1016/j.egypro.2009.01.116.
- (4) Chowdhury, F. A.; Yamada, H.; Higashii, T.; Goto, K.; Onoda, M. CO2 Capture by Tertiary Amine Absorbents: A Performance Comparison Study. *Ind. Eng. Chem. Res.* 2013. https://doi.org/10.1021/ie400825u.
- Park, H. S.; Jung, Y. M.; You, J. K.; Hong, W. H.; Kim, J. N. Analysis of the CO2 and NH3 Reaction in an Aqueous Solution by 2D IR COS: Formation of Bicarbonate and Carbamate. *J. Phys. Chem. A* 2008. https://doi.org/10.1021/jp800991d.
- (6) Hiyoshi, N.; Yogo, K.; Yashima, T. Adsorption Characteristics of Carbon Dioxide on Organically Functionalized SBA-15. *Microporous Mesoporous Mater.* 2005. https://doi.org/10.1016/j.micromeso.2005.06.010.
- (7) Bacsik, Z.; Zhang, P.; Hedin, N. Ammonium-Carbamate-Rich Organogels for the Preparation of Amorphous Calcium Carbonates. *Minerals* 2017.

11

https://doi.org/10.3390/min7070110.

- (8) Furer, V. L. The IR Spectra and Hydrogen Bonding of Toluene-2,6-Bis(Methyl) and 4,4' Diphenylmethane-Bis(Methyl) Carbamates. J. Mol. Struct. 2000.
   https://doi.org/10.1016/S0022-2860(99)00321-X.
- (9) Wang, X.; Schwartz, V.; Clark, J. C.; Ma, X.; Overbury, S. H.; Xu, X.; Song, C. Infrared Study of CO 2 Sorption over "Molecular Basket" Sorbent Consisting of Polyethylenimine-Modified Mesoporous Molecular Sieve. J. Phys. Chem. C 2009. https://doi.org/10.1021/jp809946y.
- (10) Byrnes, S. J. Multilayer Optical Calculations ArXiv: 1603.02720v2 [Physics. Comp-Ph]
  [ 28 Aug 2016. Arxiv 2016.
- Ju, L.; Geng, B.; Horng, J.; Girit, C.; Martin, M.; Hao, Z.; Bechtel, H. A.; Liang, X.; Zettl,
   A.; Shen, Y. R.; et al. Graphene Plasmonics for Tunable Terahertz Metamaterials. *Nat. Nanotechnol.* 2011. https://doi.org/10.1038/nnano.2011.146.
- (12) Zhang, S.; Kang, P.; Ubnoske, S.; Brennaman, M. K.; Song, N.; House, R. L.; Glass, J. T.; Meyer, T. J. Polyethylenimine-Enhanced Electrocatalytic Reduction of CO2 to Formate at Nitrogen-Doped Carbon Nanomaterials. *J. Am. Chem. Soc.* 2014. https://doi.org/10.1021/ja5031529.