

## Electronic Supplementary Information

### Tuning Quantum Capacitances in 2D graphene electrodes: The Role of Defects and Charge Carriers Concentration

Ayaz Hassan<sup>1</sup>, Isabela A. Mattioli<sup>2</sup>, Rafael N. P. Colombo<sup>2</sup>, and Frank N. Crespilho<sup>2\*</sup>

<sup>1</sup>*Interdisciplinary Research Center in Biomedical Materials COMSATS University Islamabad, Lahore Campus, 1.5 KM Defense Road Off Raiwind Road, Lahore, Pakistan*

<sup>2</sup>*São Carlos Institute of Chemistry, University of Sao Paulo, Sao Carlos, SP-13560-970, Brazil.*

E-mail: [frankcrespilho@iqsc.usp.br](mailto:frankcrespilho@iqsc.usp.br)

#### Contents

1. Chemicals .....	2
2. Fabrication of graphene electrodes and potentiostatic electrochemical oxidation .....	2
3. Optical microscopy and micro-Raman spectroscopy .....	5
4. Quantification of density of defects ( $n_D$ ) from micro-Raman spectra .....	5
5. Electrochemical experiments .....	8
6. References .....	8

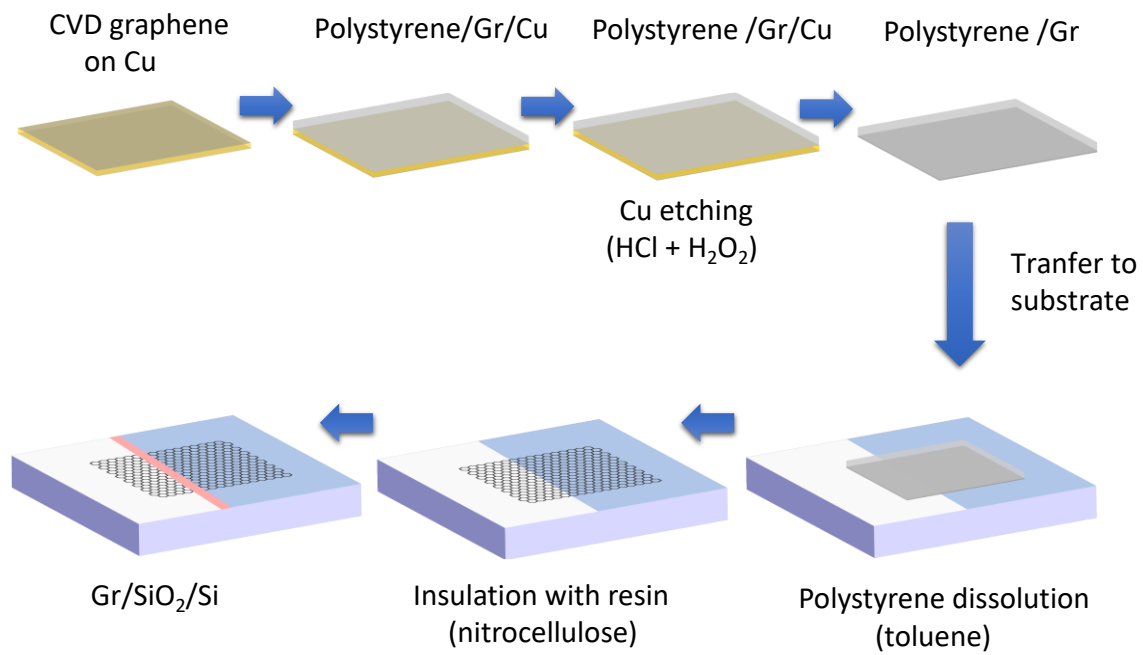
## 1. Chemicals

Monolayer chemical vapor deposition (CVD) grown graphene on Cu substrate and SiO<sub>2</sub>/Si wafer (*p*-doped, oxide thickness = 90 nm) were purchased from Graphene supermarket. Polystyrene (PS) (M<sub>w</sub> = 192,000 g mol<sup>-1</sup>), Toluene (≥99.9%), HCl (37%) H<sub>2</sub>O<sub>2</sub> (30 wt.% in H<sub>2</sub>O), K<sub>3</sub>Fe(CN)<sub>6</sub> (99%), K<sub>4</sub>Fe(CN)<sub>6</sub>·3H<sub>2</sub>O (≥99.99%), and KCl (≥99%) were obtained from Sigma-Aldrich. H<sub>2</sub>SO<sub>4</sub> (98%) was obtained from Synth.

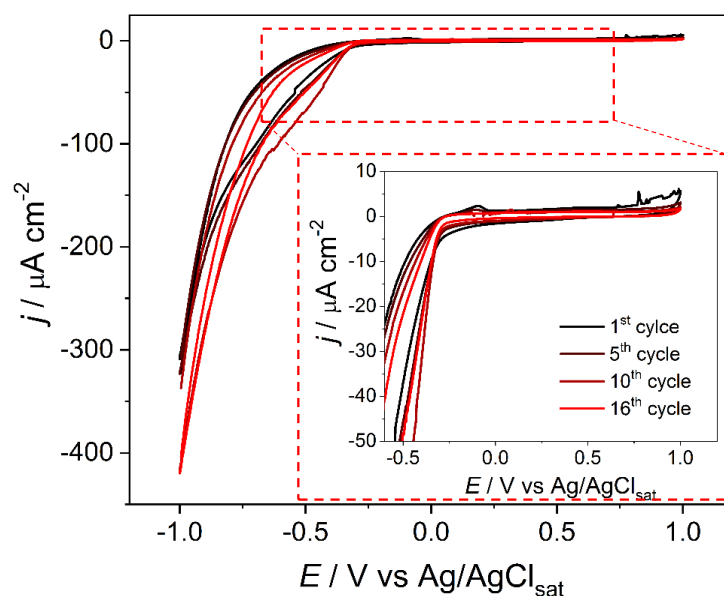
## 2. Fabrication of graphene electrodes and potentiostatic electrochemical oxidation

The monolayer graphene (CVD grown) from the Cu foil (Graphene supermarket) was transferred to the SiO<sub>2</sub>/Si substrates through a polymer-mediated transfer procedure <sup>[1,2]</sup>. Briefly, polystyrene (M<sub>w</sub>: 192,000 g mol<sup>-1</sup>) solution in toluene (50 mg mL<sup>-1</sup>) was drop-cast onto a small rectangular piece of graphene on Cu (~ 0.1 cm<sup>2</sup>) followed by drying in an oven for 10 min at 75 °C (Figure S1). Next, the Cu was removed in an etching solution of HCl (1.4 mol L<sup>-1</sup> and H<sub>2</sub>O<sub>2</sub> (0.5 mol L<sup>-1</sup>). Subsequently, the graphene on polystyrene was transferred to SiO<sub>2</sub>/Si substrate, previously modified with a metallic electrical contact (Ti (10nm)/Pt (20 nm)) and heated at 90 °C for 15 minutes. Next, the polystyrene was dissolved in toluene, leaving behind the graphene supported on SiO<sub>2</sub>/Si substrate. The obtained graphene electrode was annealed at 585 °C for one minute under an inert atmosphere (Ar). Part of the electrode in the border region between graphene and electrical contact was insulated with nitrocellulose resin to ensure that the electrolyte stayed in contact only with the graphene surface. Finally, the Cu residues left on the graphene surface during the transfer process were removed through cyclic voltammetry by cycling the electrode for 16 cycles in the potential range from -1.0 to +1.0 V in HCl (0.1 mol L<sup>-1</sup>) at 100 mV s<sup>-1</sup> <sup>[1]</sup> (Figure S2). The oxidized graphene electrodes were prepared through an electrochemical oxidation procedure by applying a potential of +2.0 V vs. Pt foil electrode to the pristine graphene electrode in the two-electrode configuration in the nitric acid (HNO<sub>3</sub>, 2.0 mol L<sup>-1</sup>) electrolyte solution in the time range from 100 to 400 s with

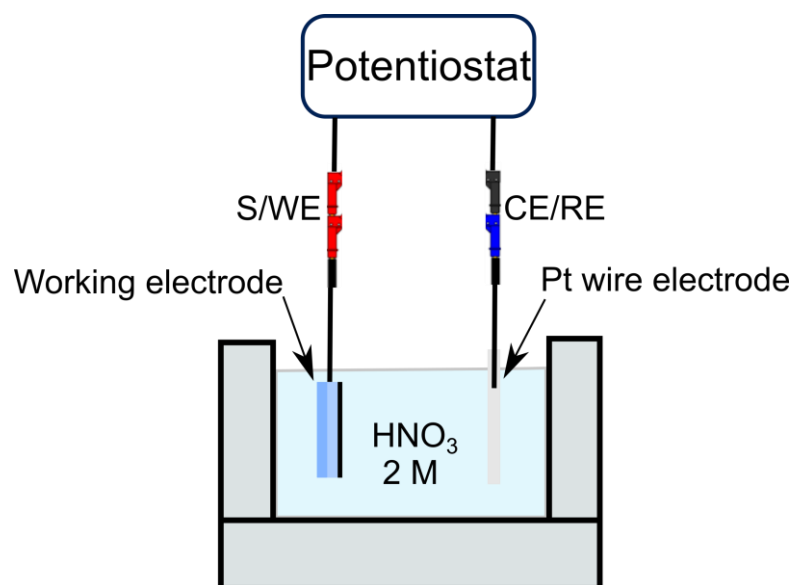
intervals of 100 s (Figure S3). This methodology was adapted from the literature, which describes the effectiveness of the  $\text{HNO}_3$  in inserting oxygen functional groups into the graphitic structure<sup>[3,4]</sup>.



**Figure S1:** Schematic of the transfer procedure of monolayer graphene to the  $\text{SiO}_2/\text{Si}$  substrate through polymer-mediated transfer<sup>[5]</sup>.



**Figure S2:** Cyclic voltammogram obtained during the electrochemical etching (e-etching)<sup>[6]</sup> of Gr/SiO<sub>2</sub>/Si electrode in HCl (0.1 mol L<sup>-1</sup>) in the potential range of -1.0 – + 1.0 V vs. Ag/AgCl<sub>sat</sub>. Scan rate: 100 mV s<sup>-1</sup>



**Figure S3:** Schematic of the electrochemical setup used for the potentiostatic (i.e., +2.0 V) electrooxidation of graphene electrodes in the nitric acid (2 mol L<sup>-1</sup>) electrolyte solution.

### 3. Optical microscopy and micro-Raman spectroscopy

Optical microscopic images were obtained for pristine and oxidized graphene electrodes using an FTIR microscope (Bruker, Hyperion 3000) coupled with a 15× microscopic objective. The micro-Raman measurements were performed in a micro-Raman spectrometer (Horiba Scientific, Model LabRam Evolution®) coupled with a microscope (Leica) and equipped with a charge coupled device (CCD) detector. The excitation wavelength used was 633 nm. Using a 100× objective lens, it was possible to collect spectra with 1 μm spatial resolution.

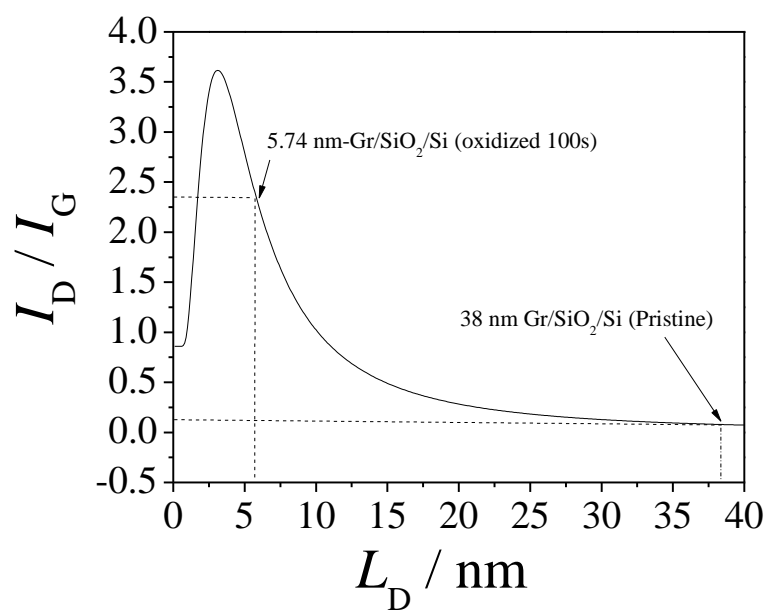
### 4. Quantification of density of defects ( $n_D$ ) from micro-Raman spectra

For the determination of the density of defects ( $n_D$ ) after the appearance of the D-band in the Raman spectra of the electrochemically oxidized graphene electrodes, the intensity ratio of the D- to G peak (i.e.,  $I_D/I_G$ ) is utilized. From the values of  $I_D/I_G$  (Table S1), the  $n_D$  values are calculated for pristine and electrodes oxidized for different duration of time by using the equation below<sup>[7,8]</sup>:

$$\frac{I_D}{I_G} = C_A \cdot \frac{r_a^2 - r_s^2}{r_a^2 - 2r_s^2} \left[ \exp\left(\frac{-\pi \cdot r_s^2}{L_D^2}\right) - \exp\left(\frac{-\pi(r_a^2 - r_s^2)}{L_D^2}\right) \right] + C_S \cdot \left[ 1 - \exp\left(\frac{-\pi \cdot r_s^2}{L_D^2}\right) \right] \quad S1$$

Where  $L_D$  represents the distance between the two adjacent defects,  $r_s$  and  $r_a$  correspond to the radii of the structurally damaged and activated region around each defective site, respectively. The values of parameters used in the above equation are  $C_A = 5$ ,  $C_S = 0.86$ ,  $r_a = 1.8$  nm, and  $r_s = 1$  nm, which are based on the excitation wavelength used (633 nm). The plot obtained by simulating the equation (Figure S4), correlates the  $I_D/I_G$  to the distance between the defects ( $L_D$ ) and can be used to determine the quality of the graphene electrodes<sup>[7,8]</sup>. Based on the  $L_D$  values obtained from the corresponding plot, the defect density values ( $n_D$ ) are calculated using the following equation (S2), as shown in Table S1.

$$n_D = \frac{10^{14}}{\pi L_D^2} \quad S2$$



**Figure S4** – Fitted  $I_D/I_G$  ratio as a function of the mean distance between defects ( $L_D$ ) for the Gr/Au/SiO<sub>2</sub>/Si and Gr/SiO<sub>2</sub>/Si electrodes.

**Table S1:** Values of parameters obtained from the micro-Raman spectra of the pristine and electrodes oxidized for different duration of time.

<b>Electrode</b>	<b>Peak Intensity D-band)</b>	<b>Peak Intensity (G-band)</b>	<b>Peak Intensity (2D-band)</b>	<b><math>I_D/I_G</math></b>	<b><math>n_D</math></b>
Gr/SiO <sub>2</sub> /Si pristine	6.03	57.18	36	0.14±0.03	$1.86 \times 10^{11} \pm 0.42$
Gr/SiO <sub>2</sub> /Si Oxidized (100s)	143	40	23	2.34±1.45	$3.56 \times 10^{12} \pm 2.39$
Gr/SiO <sub>2</sub> /Si Oxidized (200s)	189	44	23	3.09±1.51	$4.97 \times 10^{12} \pm 2.79$
Gr/SiO <sub>2</sub> /Si Oxidized (300s)	222	44	17	3.83±1.13	$6.11 \times 10^{12} \pm 2.87$
Gr/SiO <sub>2</sub> /Si Oxidized (400s)	250	48	23	3.92±1.11	$7.13 \times 10^{12} \pm 2.30$

## 5. Electrochemical experiments

A three-electrode electrochemical setup controlled by potentiostat/galvanostat ( $\mu$ AUTOLAB III/FRA2, Metrohm Autolab) was used for the electrochemical measurements. An Ag/AgCl<sub>sat</sub> reference and Pt plate as counter electrodes were used. The working electrodes were Gr/SiO<sub>2</sub>/Si. The graphene electrodes were characterized electrochemically through cyclic voltammetry experiments. For this cyclic voltammetry in [Fe(CN)<sub>6</sub>]<sup>4-</sup>/[Fe(CN)<sub>6</sub>]<sup>3-</sup> ( $1.0 \times 10^{-3}$  mol L<sup>-1</sup>) and KCl (0.1 mol L<sup>-1</sup>) was performed in the potential range from -0.6 to +0.6 V at 50 mV s<sup>-1</sup>. The electrodes were also characterized by electrochemical impedance spectroscopy (EIS) in the same electrolyte solution as used for the cyclic voltammetry experiments. The EIS experiments were performed in the frequency range from 100 kHz to 0.1 Hz. An ac amplitude of 5 mV and DC potential of 0.3 V (i.e., open cell potential) were used. The capacitance vs. potential curves were obtained by performing the alternating current (AC) cyclic voltammetry in the three-electrode electrochemical setup, with 0.1 mol L<sup>-1</sup> KCl as the electrolyte. The parameters used during these experiments were as follow: ac modulation amplitude = 10 mV, frequency = 75 Hz, and potential range = -0.5 to +0.5 V. All the applied potentials were referenced to Ag/AgCl<sub>sat</sub> reference electrode.

## 6. References

- [1] R. M. Iost, F. N. Crespilho, L. Zuccaro, H. K. Yu, A. M. Wodtke, K. Kern, K. Balasubramanian, *ChemElectroChem* **2014**, *1*, 2070.
- [2] A. Yadav, R. M. Iost, T. J. Neubert, S. Baylan, T. Schmid, K. Balasubramanian, *Chem. Sci.* **2019**, *10*, 936.
- [3] O. Jankovský, M. Nováček, J. Luxa, D. Sedmidubský, M. Boháčová, M. Pumera, Z. Sofer, *Chem. - A Eur. J.* **2017**, *23*, 6432.
- [4] L. R. Radovic, C. V. Mora-Vilches, A. J. A. Salgado-Casanova, A. Buljan, *Carbon N. Y.* **2018**, *130*, 340.
- [5] Y. C. Lin, C. Jin, J. C. Lee, S. F. Jen, K. Suenaga, P. W. Chiu, *ACS Nano* **2011**, *5*,



2362.

- [6] R. M. Iost, F. N. Crespilho, L. Zuccaro, H. K. Yu, A. M. Wodtke, K. Kern, K. Balasubramanian, *ChemElectroChem* **2014**, *1*, 2070.
- [7] M. M. Lucchese, F. Stavale, E. H. M. Ferreira, C. Vilani, M. V. O. Moutinho, R. B. Capaz, C. A. Achete, A. Jorio, *Carbon N. Y.* **2010**, *48*, 1592.
- [8] L. G. Cançado, A. Jorio, E. H. M. Ferreira, F. Stavale, C. A. Achete, R. B. Capaz, M. V. O. Moutinho, A. Lombardo, T. S. Kulmala, A. C. Ferrari, *Nano Lett.* **2011**, *11*, 3190.