Electronic Supplementary Material (ESI) for Nanoscale.

Process to enhance the specific surface area and capacitance of hydrothermally reduced graphene oxide

Amira Alazmi,[a] Omar El Tall,[b] Shahid Rasul[a], Mohamed N. Hedhili,[c] Shashikant P. Patole[a] and Pedro M. F. J. Costa[a]

[a] King Abdullah University of Science and Technology (KAUST), Physical Science and Engineering Division, Thuwal 23955-6900, Saudi Arabia. Email: pedro.dacosta@kaust.edu.sa

[b] King Abdullah University of Science and Technology (KAUST), Analytical Core Laboratory, Thuwal 23955-6900, Saudi Arabia

[c] King Abdullah University of Science and Technology (KAUST), Imaging and Characterization Laboratory, Thuwal 23955-6900, Saudi Arabia.

Supporting Information

1. Experimental Section

1.1. Drying equipment

The vacuum drying process was performed in a Thermo Scientific Lindberg Blue M vacuum oven. For the freeze drying process, a Labconco Freezone 2.5plus was used. Finally, the critical point drying was performed in a Leica EM CPD300.

1.2. Characterisation

The powder X-ray diffraction (XRD) analysis was performed on a diffractometer (Bruker D8 Advance) with Cu K_α radiation ($\lambda = 1.5418$ Å). The morphology of the samples was observed with scanning electron microscopy (SEM) (FEI Quanta 600, 4 kV). N_2 adsorption-desorption measurements were conducted at 77 K with a Micromeritics ASAP 2420 instrument. Prior to the analysis, the samples were degassed under vacuum at 80 °C for at least 12 h. The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) method. The pore size distribution analysis in the mesopore range was performed using the Barrett-Joyner-Halenda. (BJH) formulism applied to the isotherm adsorption branch, and the full micro-meso pore size distribution was calculated using the DFT model assuming slit pores using the Microactive Interactive data analysis software. X-ray photoelectron spectroscopy (XPS) studies were carried out in a Kratos Axis Ultra DLD spectrometer equipped with a monochromatic Al Kα X-ray source (hν = 1486.6 eV) operating at 150 W, a multi-channel plate and delay line detector under a vacuum of ~10^{-9} mbar. The survey and high-resolution XPS spectra were collected at fixed analyzer pass energies of 160 eV and 20 eV, respectively. Samples were mounted in floating mode in order to avoid differential charging. Binding energies were referenced to the sp^2 hybridized (C=C) carbon for the C 1s peak set at 284.4 eV.

1.3. Electrochemical characterisation

For the electrochemical characterization, the working electrodes were prepared by mixing ~2 mg of the selected rGO with 15 µl of Nafion (Sigma-Aldrich, 5 wt.%), 500 µl of deionized water (MilliQ, 18.2 MΩ·cm) and 500 µl of ethanol (Sigma-Aldrich, >99.8). The mixture was ultrasonicated for 30 min to form a homogenous slurry. The slurry was drop-cast onto the glassy carbon electrode (3 mm diameter) and dried under an incandescent bulb lamp for ~10 min. All electrochemical experiments were carried out in 1 M H_2SO_4 at room temperature using a three-electrodes system, in which a Pt wire and a standard calomel electrode (SCE) were used as the counter and reference electrodes, respectively. Cyclic voltammetry (CV), at scan rates of 100 mV s^{-1}, and galvanostatic charge-discharge runs were carried out using a BioLogic VMP3 electrochemical workstation. The specific capacitance was calculated from the CV and discharging curves according to the following equation:

$$C_{sp} = (I \times \Delta t)/(\Delta V \times m) \tag{1}$$

Where C_{sp} (F g^{-1}) is the specific capacitance of the electrode, I (A) is the discharging current, Δt (s) is the discharging time, ΔV (V) is the potential and m (g) is the mass of the rGO.

2. Results

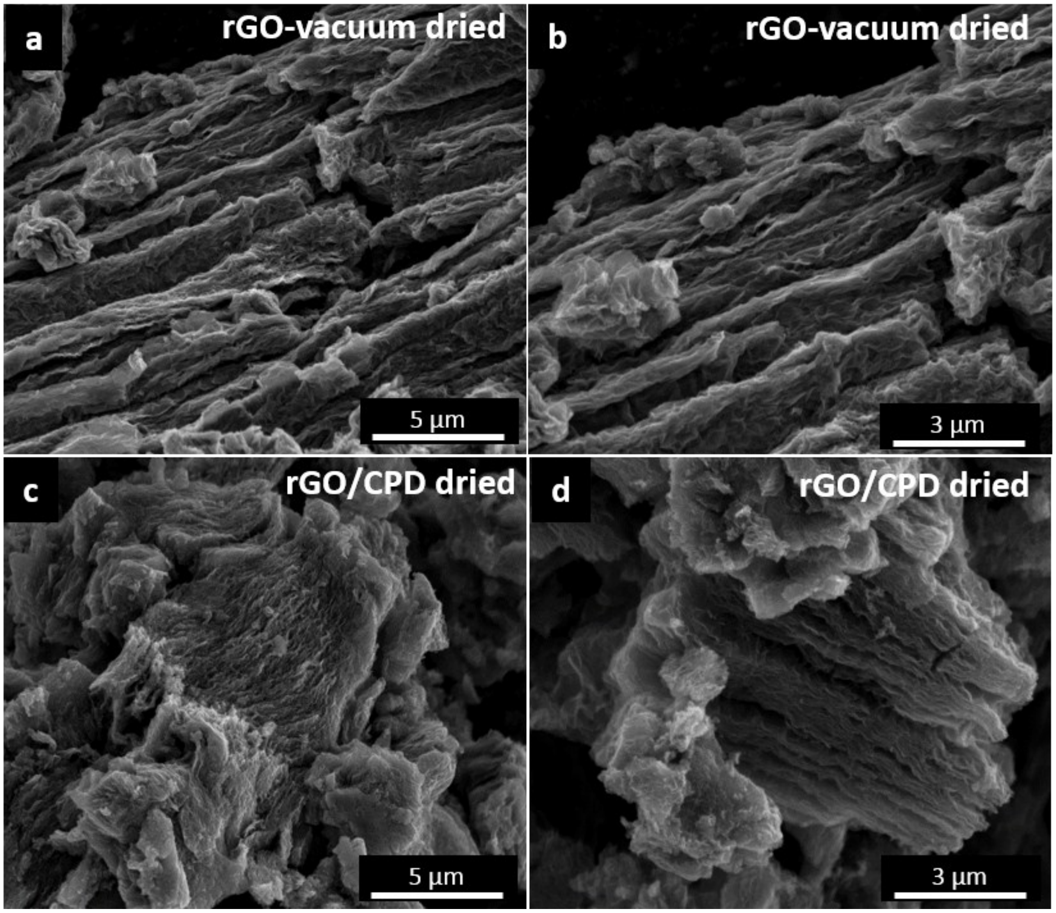

Figure S1. SEM images of the (a - b) rGO/vacuum and (c - d) rGO/CPD samples. It is easily recognizable that the separation of the layers in the CPD product is more regular/homogenous across the entire sample, i.e. not restricted to a particular aggregate or parts of this.

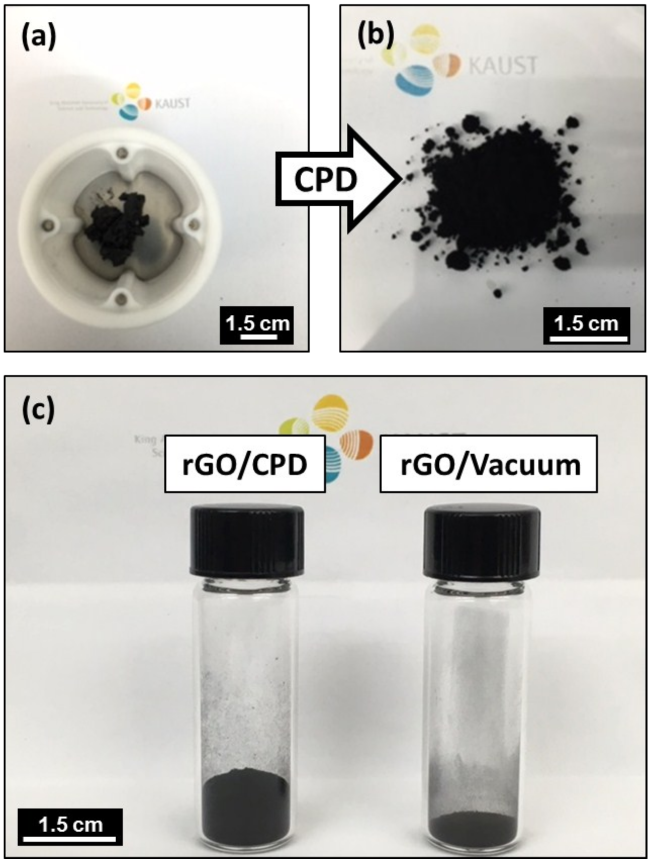

Figure S2. Digital photos of: (a) the wet rGO, (b) the rGO in (a) after CPD processing, (c) two vials with 100 mg each of dried rGO products – the higher volume occupied by the rGO/CPD is notable.

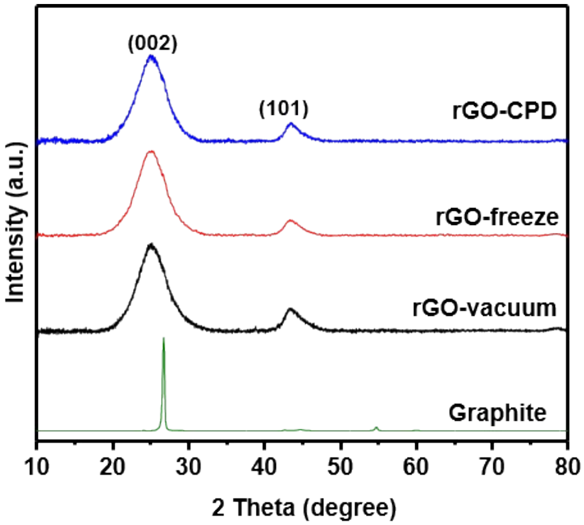

Figure S3. Powder XRD patterns of the graphite precursor, rGO/vacuum, rGO/freeze and rGO/CPD samples. The rGOs have equal spectra precluding therefore structural dissimilarities.

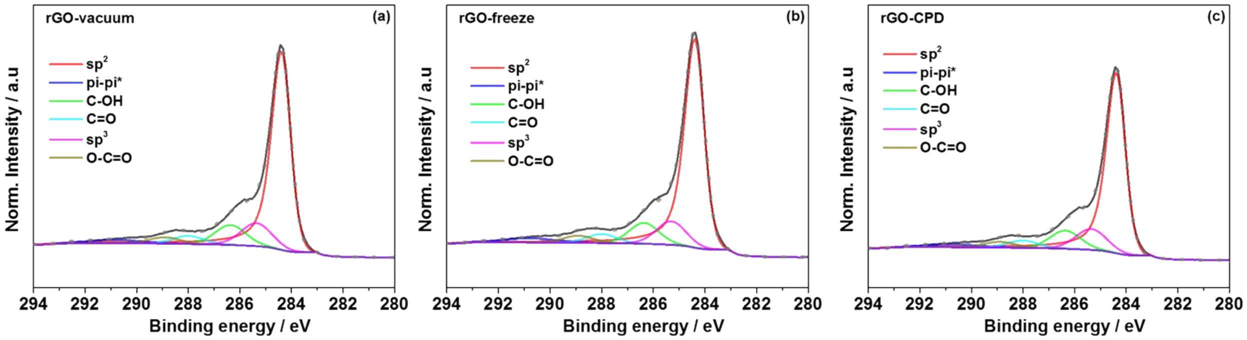

Figure S4. High resolution XPS C1s spectra of (a) rGO/CPD, (b) rGO/freeze and (c) rGO/vacuum samples. The deconvolution of the C1s peak confirms the equivalent chemical identity in the three samples. The high-resolution C 1s spectrum was convoluted for rGO/vacuum, rGO/freeze and rGO/CPD. The spectrum shows an intense peak of C=C (sp^2 arrangement) located at 284.4 eV. Besides the C=C peak, the C 1s spectrum deconvolution identified five other bands: sp^3 (285.3 eV), C-OH (286.4 eV), C=O (288.0 eV), O-C=O (288.9) and the π-π* satellite peak (290.8 eV). The relative concentration (atomic %) of the components was calculated using the CasaXPS software: C=C 65%, sp^3 13%, C-OH 11%, C=O 5%, O-C=O 3% and Pi-Pi* 3%.

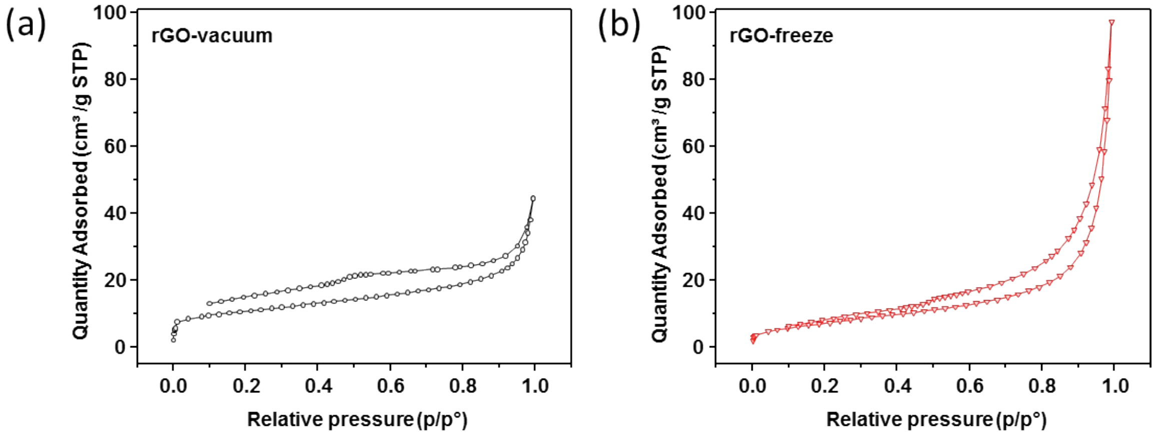

Figure S5. Nitrogen adsorption–desorption isotherms of: (a) rGO-vacuum, (b) rGO-freeze.

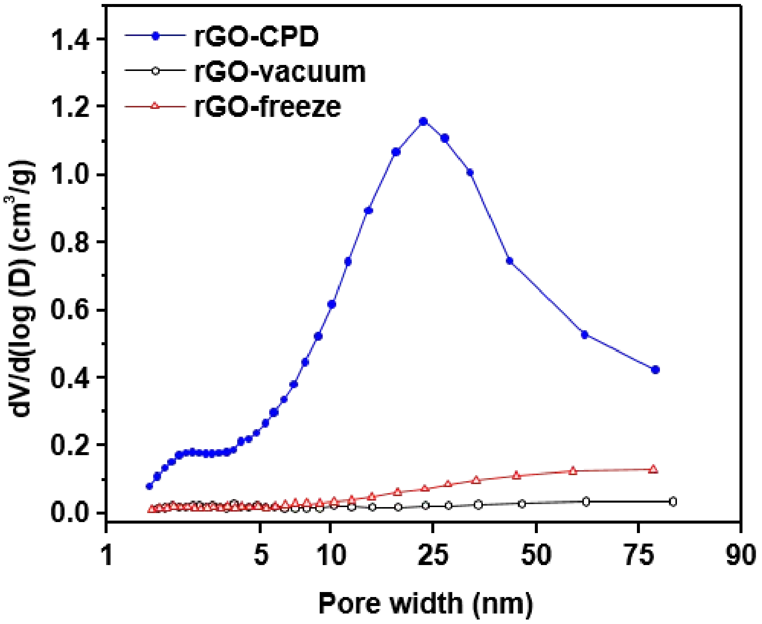

Figure S6. Pore-size distribution profiles from adsorption of N_2 on the studied rGO materials (calculated using the BJH method).

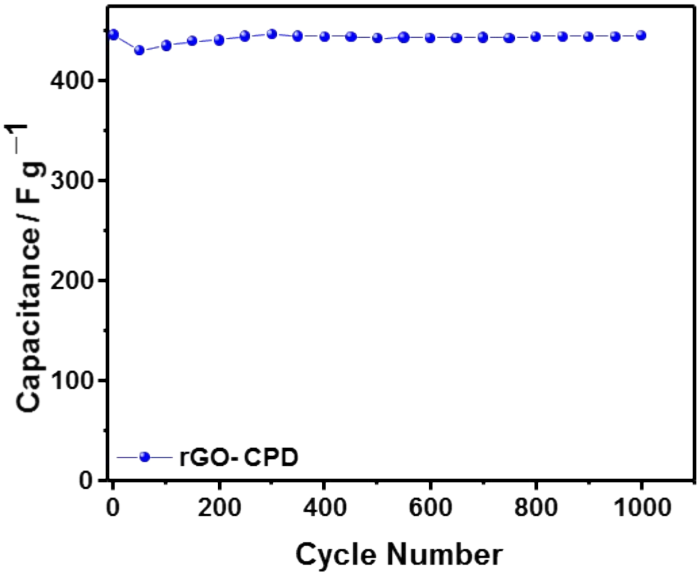

Figure S7. Cyclic performance of a rGO/CPD sample, at a current density of 1 A g^{-1} in H_2SO_4. The capacitance is well retained throughout, at more than 400 F g^{-1}.

Table SI-1. Specific surface areas reported in the literature for rGO using the hydrothermal reduction method.

Surface area (m^2/g)	Reference
102	J. Solid State Electrochem., 19 (2014), 361.
62	RSC Adv., 4 (2014), 42412.
31	Appl. Surf. Science, 358 (2015), 100.
364	This work

Table SI-2. Electrochemical performance of rGOs reported in the literature.

Reduction method	Specific capacitance (Fg^{-1})	Reference
Solvothermal (dried in vacuum)	276 @ 0.1 Ag^{-1}	J. Phys. Chem. C, 115 (2011), 7120.
Thermal	227 @ 1 Ag^{-1}	Carbon, 50 (2012), 2179.
Thermal	261 @ 0.4 Ag^{-1}	J. Power Sources, 198 (2012), 423.
Hydrothermal (dried at 60°C)	139 @ 5 Ag^{-1}	J. Mater. Chem., 21 (2011), 3422.
Hydrothermal (dried at 60°C under vacuum)	90 @ 5mA cm^{-2}	Russian J. Electrochem., 49 (2013), 359-364.
Hydrothermal (dried by CPD)	441 @ 1 Ag^{-1}	This work