Supporting information for

# Vortex fluidic mediated transformation of graphite into highly conducting graphene scrolls

Kasturi Vimalanathan,[a] Irene Suarez-Martinez,[b] Chandramalika Peiris,[c] Joshua Antonio,[c] Carla de Tomas,[b] Yichao Zou,[d] Jin Zou,[d] Xiaofei Duan,[e] Robert N. Lamb,[e] David P. Harvey,[a] Thaar M.D. Alharbi,[a] Christopher T. Gibson,[a,f] Nigel Marks,[b] Nadim Darwish[c*] and Colin L. Raston [a*]

a Flinders Institute for Nanoscale Science & Technology, College of Science and Engineering, Flinders University, Adelaide SA 5001, Australia

b Nanochemistry Research Institute, Department of Physics and Astronomy, School of Science, Curtin University, Bentley Campus, Perth, WA 6102, Australia

c School of Molecular and Life Sciences, Curtin Institute of Functional Molecule and Interfaces, Curtin University, Bentley WA 6102, Australia.

d School of Mechanical and Mining Engineering and Centre for Microscopy and Microanalysis, The University of Queensland, Brisbane, QLD 4072, Australia

e Trace Analysis for Chemical, Earth and Environmental Sciences (TrACEES), The University of Melbourne, Victoria 3010, Australia

f Flinders Microscopy and Microanalysis, College of Science and Engineering, Flinders University, Adelaide, South Australia 5042, Australia

*Corresponding author email: colin.raston@flinders.edu.au and nadim.darwish@curtin.edu.au

**Experimental method:**

**Fabrication of graphene scrolls in the VFD.** In a typical experiment, graphite flakes (1 mg, particles size 7-10 µm in lineal dimension of the planar flakes) were dispersed in toluene (0.5 mg/mL). MilliQ water (0.5 mL) was then added to the graphite/toluene dispersion (0.5 mL) in a borosilicate glass tube (20 mm OD, 17.50 ± 0.013 mm ID). The volume ratio of the graphite/toluene dispersion to water was optimised to a 1:1 ratio. The optimum confined mode VFD operating parameters for generating high yield graphene scrolls were θ at 45$^{o}$ and rotational speed set at 7500 rpm for a reaction time of 30 minutes. Centrifugation (g=3.22) of the post-processed material for 30 minutes removed residual graphite flakes, which can be recycled, and any contaminants present in the sample.

**Characterization.** The graphene scrolls were characterized by Field Emission SEM (FEI Quanta 450, operated at 5 kV at a working distance of 10 mm), AFM (Nanoscope 8.10 tapping mode), TEM (JEOL JEM-2100F, operated at 200 kV and equipped with an EDS detector), Raman spectroscopy and thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Raman scattering were recorded at an excitation wavelength of 532 nm (≤ 5mW) at room temperature. TGA and DSC were performed as a simultaneous thermal analysis (STA) on a Perkin Elmer STA800. The sample was heated from room temperature to 840 ºC at a rate of 10 ºC/min under an atmosphere of $N_2$ (20 ml/min). To examine the change in heat flow at 450 ºC on scroll structure the experiment was repeated but terminated at 500 ºC, the resultant product was then examined using SEM methods described above. Samples for SEM and Raman analysis were prepared on clean silicon wafers. TEM specimens were prepared by drop-casting the dispersion of graphene scrolls onto standard holey carbon grids prior to characterization. X-ray photoelectron spectroscopy (XPS) analysis was carried out using the Kratos Axis Ultra, Thermo Scientific, UK, with monochromatic Al *Ka* X-rays.

**Tapping mode AFM**

Atomic force microscopy (AFM) was performed in air using a Bruker Multimode 8 AFM with Nanoscope V controller, operating in standard tapping mode. The AFM probes used were silicon HQNSC15/AlBS Mikromasch probes (nominal tip diameter and spring constant is 16 nm and 40 N/m respectively). Set-point, scan rate and gain values were chosen to optimize image quality. The AFM topography images have been flattened and height measurements were made using the section analysis tool of Nanoscope Analysis 1.4. The AFM scanner was calibrated in x,y and z directions using silicon calibration grids (Bruker model numbers PG: 1 µm pitch, 110 nm depth and VGRP: 10 µm pitch, 180 nm depth and Mikromasch model TGZ01: 3 µm pitch, 18 nm depth).

**Raman**

Raman spectra were acquired using a Witec alpha300R Raman microscope at an excitation laser wavelength of 532 nm with a 100x objective (numerical aperture 0.00). Typical integration times for single Raman spectra were between 30-60 s for 2-3 accumulations. The grating used was 600 grooves $mm^{-1}$ which has a spectral resolution of ~3 to 4 wavenumbers. Laser power levels were kept as low as possible to prevent sample damage and was approximately 5 mW or below.

**Conductive AFM studies**

Sample topographies and dc conductivities were imaged with a Bruker Dimension Icon atomic force microscope. Data were obtained in air at room temperature and using conductive platinum tips (Rocky Mountain Nanotechnology AFM probes, 25Pt300B, with spring constant of 18 N $m^{-1}$). The imaging resolution was set to 512 points/line, the scan rate to 0.5 Hz and the peak force setpoint to 200 nN. Current maps were collected at a sample bias of + 100 mV. The I–V curves were taken at voltage sweep rates of 1 V/s and with the feedback being switched to contact mode with the deflection set-point kept constant to 500 nN. The deflection setpoint corresponding to 500 nN was chosen such that the current through the contact becomes independent on the force.

**Computational studies**

Starting coordinates were obtained by geometrically wrapping a graphene flake into an Archimedean spiral. Periodic boundary condition applied along the scroll axis and the edges were saturated with hydrogen atoms. Molecular Dynamics (MD) simulations were performed using the LAMMPS package with the AIREBO potential. All heated structures were equilibrated at 100 K in the NVT (constant particle-volume-temperature) ensemble for 20 ps before the temperature is increased to 2000 K. In all cases angular momentum was removed every 1000 steps to avoid rotations of the entire structure. The Debye model describes the contributions of phonons to the total energy of the system, using Bose-Einstein statistics for the occupancy. Electrons make a negligible contribution and can be ignored. In most solids, a single Debye temperature is sufficient, but for scrolls two values are required; a relatively small value (120 K) for soft out-of-plane vibrations and a large value (2300 K) for stiff in-plane vibrations. Note that the latter is the two-dimensional Debye temperature of graphene. Since the Debye model describes the total energy of the system, the potential energy contribution is one-half this value due to the principle of equipartition, which splits the energy evenly between potential and kinetic energy components. Within this formalism, the contribution to the potential energy becomes

$$PE_{\text{Debye}}(T) = \frac{1}{2}\left[U(T,2300,2) + U(T,120,1)\right]$$

where U is the energy-per-atom in the Debye model according to the expression

$$U(T, T_D, d) = d2\,kBT\left(\frac{T}{TD}\right)d\sum_{0}^{T/TD}\frac{xd}{ex-1}\,dx$$

where d is the dimensionality, $T_D$ is the Debye temperature and $k_B$ is Boltzmann's constant. The integrals were determined numerically using MATLAB, and the heat-capacity was computed by differentiation to confirm that the classical limits of d $k_B$T were obtained. In the case of the low-temperature component, the phonon modes are fully occupied for most of the temperature range of interest, and hence replacing this term by its classical value of $k_B$T would have minimal effect on the predicted unrolling temperature.

**Supplementary Materials for this manuscript include the following:**

**Movie 1**. Molecular dynamics of a graphene scrolls with an initial radius larger than the optimal radius. The simulation shows the unraveling of a graphene scroll from an initial radius of 12 A which scrolls tighter to then unravel into a single layer.

**Movie 2**. Molecular dynamics of a graphene scrolls with an initial radius smaller than the optimal radius. The simulation shows the unraveling of a graphene scroll from an initial radius of 4 A.

**Supplementary information 1**

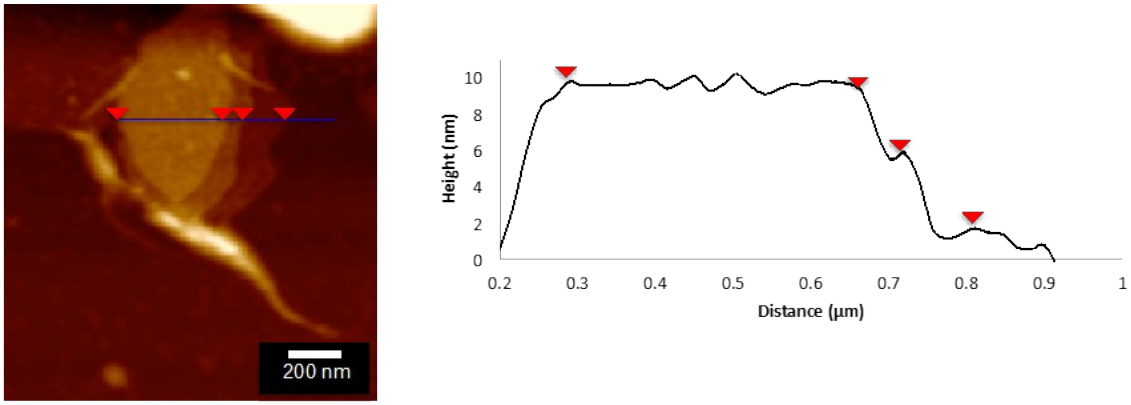


**Fig. S1**. AFM height image of small amounts of exfoliated graphene sheets present in the post processed sample and its associated height profile. Exfoliated graphene sheets (non-scrolled) were evident in the processed sample (with thicknesses ranging between 2-4 nm). The yield of the graphene scrolls afforded under the reported optimized conditions was *ca* 30% with the small amounts of exfoliated graphene sheets and graphite flakes separated via centrifugation with potential of recycling through the system to afford scrolls.

**Supplementary information 2**

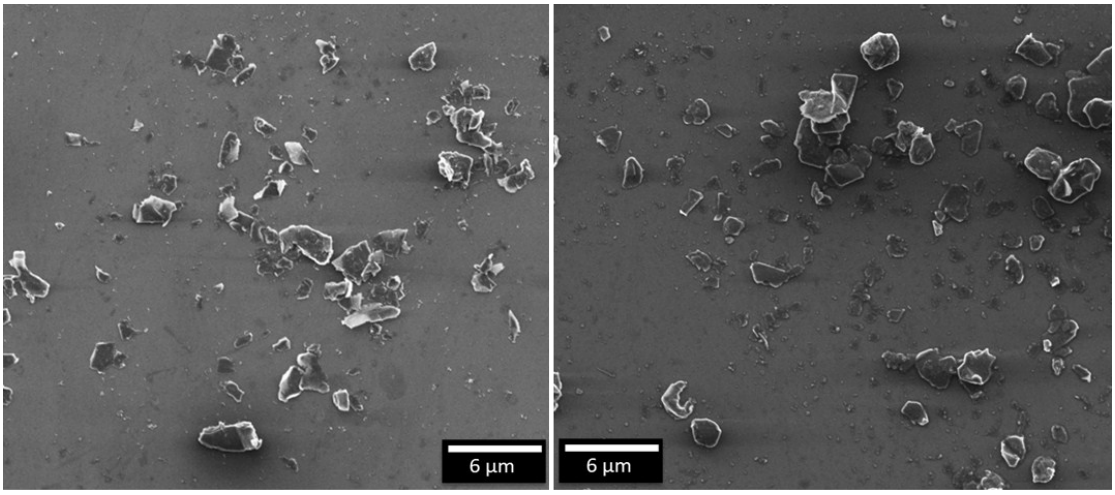


**Fig. S2. SEM images of graphite flakes processed under continuous flow for scalability purposes.**

The process involved using toluene and water as the solvent system at a 1:1 volume ratio at the optimized experimental conditions, at a concentration of 0.10 mg/mL, rotational speed of 7500 rpm, 45° inclination angle and a flow rate of 0.45 mL/min. Control experiments were carried out using a range of different flow rates, i.e. 0.1 mL/min, 0.25 mL/min, 1.0 mL/min and 2.0 mL/min. No scrolls were observed

**Supplementary information 3**

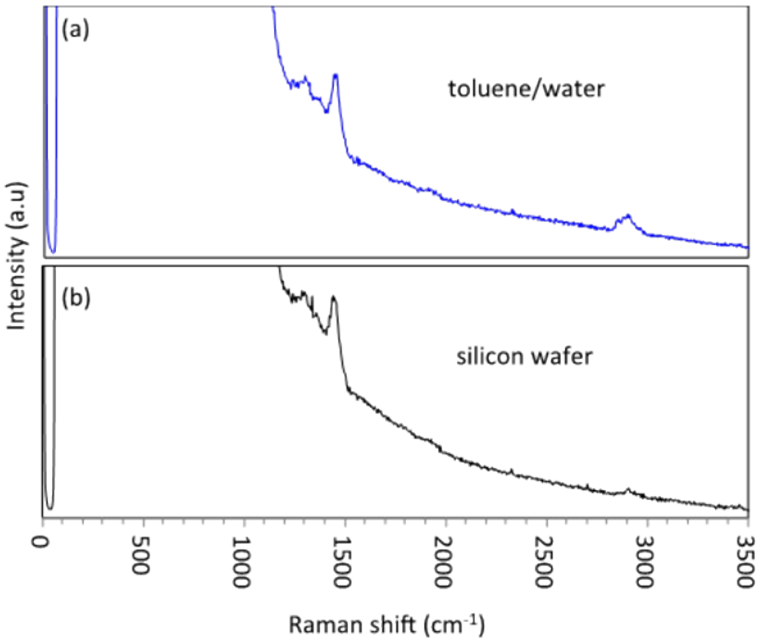


**Fig. S3**. **Control Raman spectroscopy of the immiscible solvent system (toluene/water) and just silicon wafer (substrate).** Raman spectroscopy of the control experiments for the assignment of the two additional peaks present in the graphene scroll spectra; (a) toluene/water solvent system, and (b) pure silicon wafer. Other than the D, G and 2D band typically observed for graphitic material, additional peaks were observed in the Raman spectra at approximately 1436 $cm^{-1}$ and 2870 $cm^{-1}$. Control experiments established them to correspond to the silicon substrate and the toluene/water solvent respectively.

**Supplementary information 4**

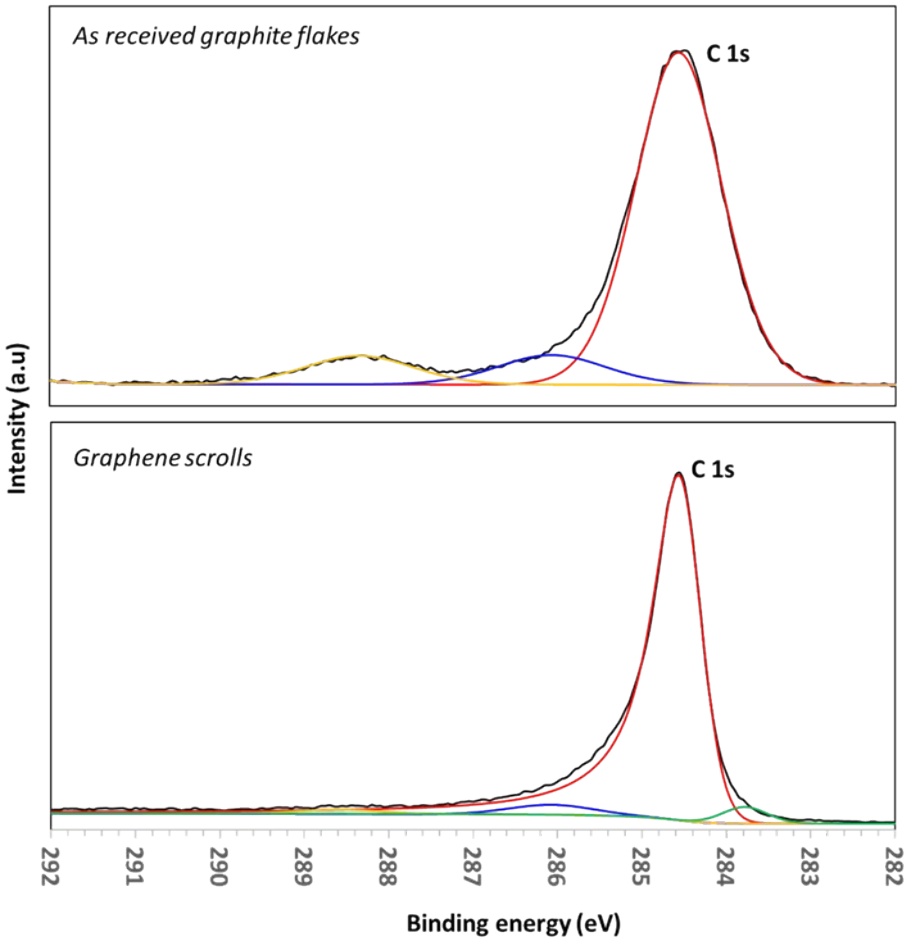


**Fig. S4. XPS spectra of the graphene scrolls compared to the as received graphite flakes.** XPS curves with binding energy peaks at 284.4 eV ($sp^2$ carbon), 286.1 eV (C-O) and 288.6 eV (O-C=O).

**Supplementary information 5**

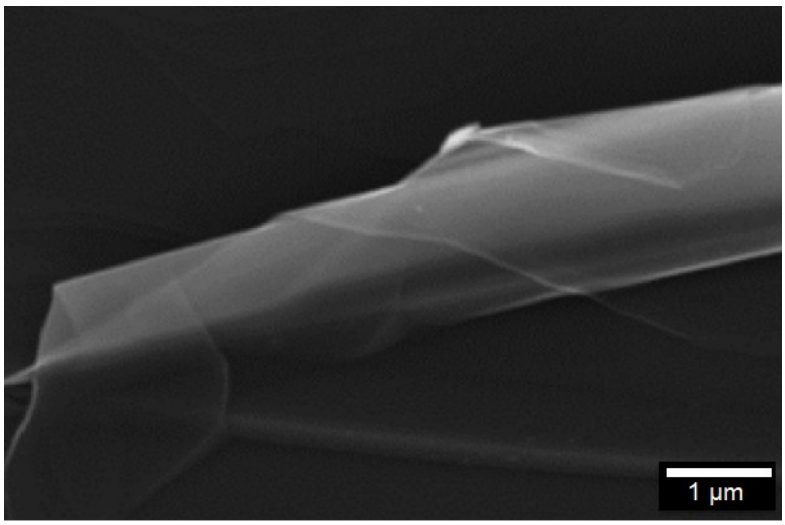


**Fig. S5. High resolution SEM.** Image of a graphene scroll deposited on a HOPG substrate prior to electrical measurements.

**Supplementary information 6**

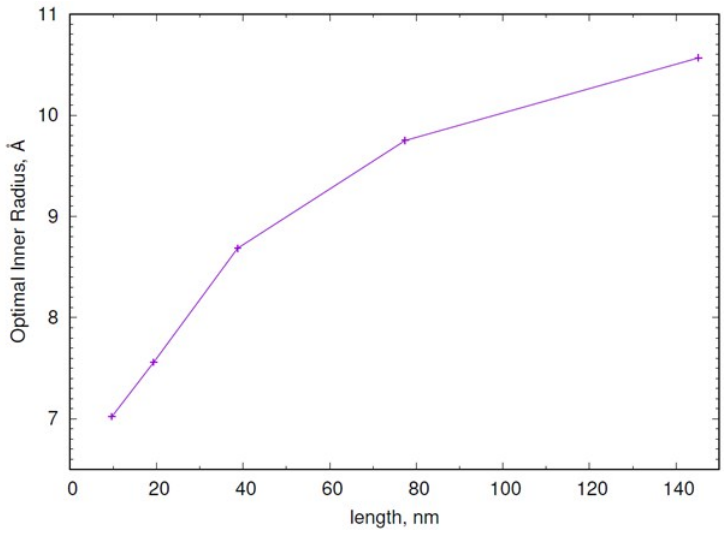


**Fig. S6**. **Single point energy calculations.** Plot of the optimal inner radius for the single point energy calculations as function of the length of the scroll.

**Supplementary information 7**

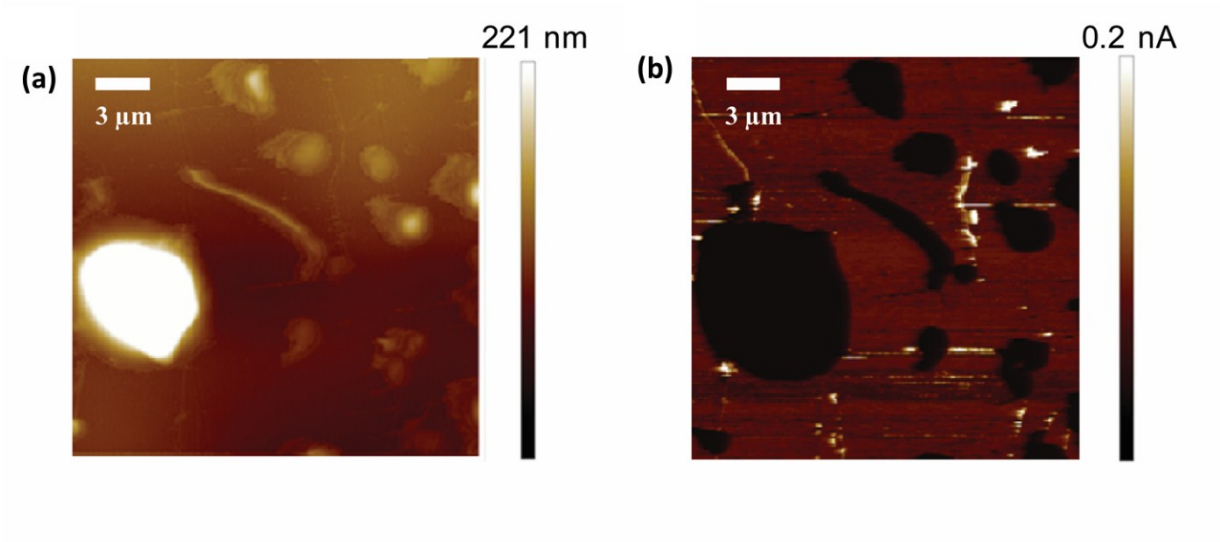


**Figure S7**. **Conducting AFM images of the starting graphite flakes.** A) Topography image of the starting material, graphite flakes, measured at the defined force of 200 nN. B) the corresponding current image.