Electronic Supplementary Material (ESI) for ChemComm.
This journal is © The Royal Society of Chemistry 2016

Electronic Supplementary Information

Plasma enhanced vortex fluidic device manipulation of graphene oxide

Darryl B. Jones,[a,b*] Xianjue Chen,[a†] Alexander Sibley,[a] Jamie S. Quinton,[a] Cameron J. Shearer,[a] Christopher T. Gibson[a] and Colin L. Raston[a,c*]

[a.] *Centre for Nanoscale Science and Technology, School of Chemical and Physical Sciences, Flinders University, GPO Box 2100, Adelaide, SA 5001, Australia.*

[b.] *E-mail: darryl.jones@flinders.edu.au*

[c.] *E-mail: colin.raston@flinders.edu.au*

† Present Address: Center for Multidimensional Carbon Materials, Institute of Basic Sciences Center, Ulsan National Institute of Science and Technology, Republic of Korea.

S.I. 1. G-O Preparation

G-O was prepared from graphite powder (SP-1, Bay Carbon) using a modified Hummer's method.[1, 2] In brief, graphite powder (6 g) was first pre-treated within a concentrated H_2SO_4 solution (25 mL) at 80 °C for 4.5 h, in the presence of $K_2S_2O_8$ (5 g) and P_2O_5 (5 g). After cooling down to room temperature, the solution was diluted with DI water, and kept standing overnight. After that, the supernatant was decanted, and the pre-treated graphite was obtained by vacuum filtration and washing with DI water. To a concentrated H_2SO_4 (250 mL) solution below 5 °C was added the pre-treated graphite powder and $KMnO_4$ (30 g). The mixture solution was stirred at 35 °C for 2 h, cooled in an ice bath, and diluted with DI water. The solution was further stirred for another 2 h, during which DI water was added, followed by addition of a H_2O_2 solution (30%, 25 mL). After the reaction the mixture was kept standing overnight, the graphite oxide was obtained by centrifugation and subjected to cycles of suspension in 10% HCl solution and separation by centrifugation. In order to remove the free acid and remaining ions, the graphite oxide was subjected to cycles of washing with DI water and separation with centrifugation until the pH value of the supernatant reached 6.

S.I. 2. Transmission Electron Microscopy (TEM)

High resolution transmission electron micrographs were obtained using a JEOL JEM-2100F transmission electron microscope (TEM) operating at the University of South Australia. TEM specimens were prepared by depositing a drop of the samples onto a holey carbon coated copper grid (#2450-AB, SPI Supplies) and dried under ambient conditions. The TEM was operated at 120 kV. Image J software was used for processing all the TEM images.

S.I. 3. X-ray Photoelectron Spectroscopy (XPS)

A survey X-ray photoelectron spectrum was obtained for each sample using a Leybold-Hereaus LHS-11 instrument. Here the specimens were deposited onto a silicon substrate. Carbon chemical bonding environment information was then obtained by measuring a high resolution C1s spectrum on each sample using the same instrument. Each C1s spectrum was then fitted using synthetic line shapes to determine information about the carbon chemical bonding environments. Here synthetic line shapes that were a mixture of Gaussian and Lorentzian functions (FWHM ~1.5eV) were used to fit each spectral components [CC/CH (C-C,C=C,CH) ~ 284.8 eV, CO (C-O-C, COH) ~ 286.6 eV, C=O ~ 287.6 eV and COOH ~ 289.1 eV]. On each sample, a Shirley background was subtracted from the measured spectrum. This analysis was performed in CASA-XPS software.[3] The silicon substrate contributes to the oxygen signal so that its intensity and shape could not contribute to a meaningful

interpretation of the G-O modifications. The nitrogen content of the N_2 plasma modified G-O was too low to investigation through high resolution XPS.

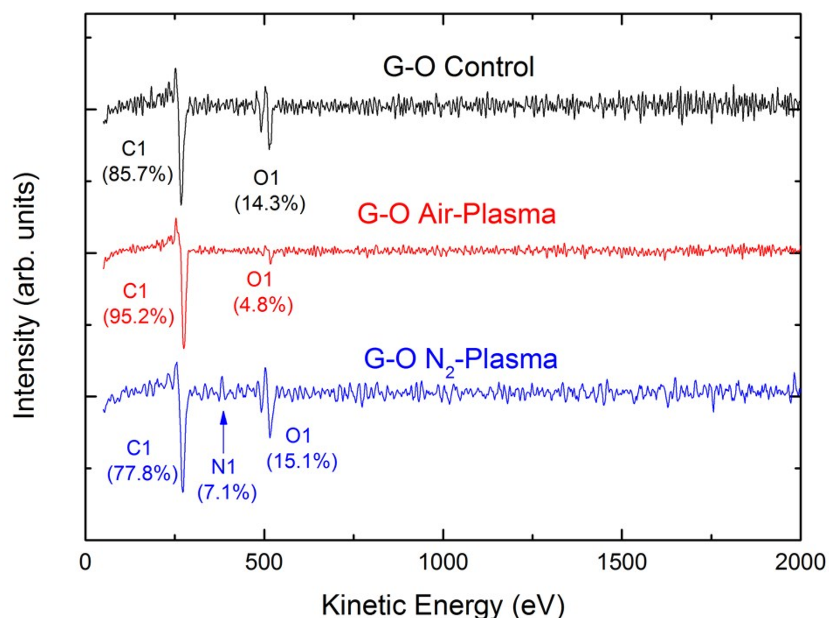
S.I. 4. Scanning Auger Electron Microscopy

Scanning electron micrographs and scanning Auger micrographs were obtained with a PHI 710 Scanning Auger Nanoprobe. Auger electron spectra were sampled for at least 4 different surface locations on each sample under 10kV/10nA or 3kV/1nA beam conditions. Example differential Auger spectra are shown in SI Fig 1. The Auger electron spectra were used to determine the average elemental composition of the untreated and plasma treated graphene oxide samples. Here the average elemental composition of each sample was obtained by averaging the scanning Auger elemental analysis of the spectra obtained at different surface locations, with the standard deviations of these measurements being used as the uncertainty. Note that only spectra with a negligible substrate contribution (Si < 1%) were used for the C/O elemental analysis. This analysis procedure avoided sampling the edges of the G-O regions, and is therefore more indicative of the basal plane C:O ratio. Note that this is different to the information obtained through the C1s XPS data which reflects all carbon environments of the G-O sample (edges and basal plane). A summary of the derived elemental compositions for each sample derived from the Auger data is contained in SI Table 1.

SI Table 1. Average elemental composition of the control, air plasma and N_2-plasma treated G-O derived using Auger Electron Spectra from different regions of each sample.

Sample	C (%)	O (%)	S(%)	N(%)	Ratio C/O
Control G-O	82.3 ± 6.6	17.7 ± 6.6	-	-	4.6 ± 1.8
Air plasma G-O	92.4 ± 2.7	7.2 ± 2.7	0.4± 0.4[(a)]	-	12.8 ± 4.8
N_2-plasma G-O	81.1 ± 5.1	18.0 ± 5.0	-	0.9± 2.5[(b)]	4.5 ± 1.3

(a) Here trace Sulphur remain from the G-O synthesis.
(b) The large uncertainty arises from the Nitrogen signal either being prominent in the spectra or not present at all.



SI Fig 1. Example differential scanning Auger spectra for a single region on each sample. These spectra were obtained at 10kV/10nA incident electron energy, and were corrected for the elemental sensitivity in determining the elemental concentrations.

S.I. 5. Raman Imaging

Raman spectral microscopy was performed using a Witec alpha300R Raman microscope with excitation laser wavelength of 532 nm (≤ 5 mW) at room temperature. The Raman images were recorded with an x40 objective lens (Numerical Aperture 0.60) with typical integration times between 3 to 5 seconds per pixel.

Optical markers from low-magnification scanning electron micrographs where used to locate regions on the sample for atomic force microscopy and Raman imaging. These regions were selected because they were near to the regions examined using the scanning Auger microscopy.

Here individual spectra from Raman imaging performed at multiple locations across samples for the original (1600 individual spectra), Air Plasma (2500 individual spectra), and N_2-plasma treated (600 individual spectra) G-O samples were collated to construct an average Raman spectrum. I_G/I_D ratios were also obtained for 30 unique spectra from each sample (with the reported uncertainty being the standard deviation). These values were found to be consistent with the I_G/I_D ratio obtained for the average spectra. These results are summarised in SI Table 2.

SI Table 2. Summary of Raman I_G/I_D Ratio.

Sample	Individually analysed Spectra[a]	Average Spectra
Control G-O	0.86 ± 0.03	0.84[b]
Air plasma G-O	0.85 ± 0.03	0.84[c]
N_2-plasma G-O	1.00 ± 0.07	0.98[d]

[a] 30 spectra; [b] 1600 spectra; [c] 2500 spectra; [d] 600 spectra.

S.I. 6. Atomic Force Microscopy (AFM)

All AFM measurements were acquired using a Bruker Dimension FastScan AFM with Nanoscope V controller, and Nanoscope control software (version 8.15). AFM images were acquired using peak-force tapping mode with all parameters including set-point, scan rate and feedback gains adjusted to optimize image quality and minimize imaging force. Images were acquired using ScanAsyst-air probes (Bruker) with nominal spring constant of 0.4 N m^{-1} and nominal tip diameter of 4 nm. AFM data was analysed using Nanoscope analysis software (version 1.4).[4] The 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).

Optical markers from low-magnification scanning electron micrographs where used to locate regions. close to those used for performing the Raman images on the sample for atomic force microscopy. The G-O topography was then analysed through height profiles and the average roughness. Here average roughness R_a of an area of an image is calculated using:

$$R_a = \frac{1}{N}\sum_{i=1}^{N}|Z_i| \tag{1}$$

Here Z_i is the height deviation of the i-th point from the mean image area data plane, where there are N-points in the area. Here the image areas included in the analysis were selected to coincide with the regions of G-O. The average roughness, obtained as the average over multiple sample locations on each sample, are summarised in SI Table 3.

SI Table 3. Average Roughness for each sample determined using AFM.

Sample	Average Roughness (nm)
Control G-O	9.9 ± 0.8
Air plasma G-O	48.5 ± 7.4
N_2-plasma G-O	4.2 ± 0.7

References

1. W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339-1339.
2. N. I. Kovtyukhova, P. J. Ollivier, B. R. Martin, T. E. Mallouk, S. A. Chizhik, E. V. Buzaneva and A. D. Gorchinskiy, *Chem. Mater.*, 1999, **11**, 771-778.
3. CasaXPS, Casa Software Ltd, http://www.casaxps.com/.
4. NanoScope Analysis v1.40 Bruker Corporation (2012).