

SUPPLEMENTARY INFORMATION

Gram-scale production of graphene based on solvothermal synthesis and sonication

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Elemental Analysis

Material	% Composition / Mass			
	C	H	N	O (By Difference)
Graphite	94.46	0.14	-	5.40
Graphene	78.49	2.69	-	18.82

X-Ray Photoemission Spectroscopy (XPS)

Material	% Composition / Mass				
	C	O	Na	Cl	S
Graphite	96.59	2.34	-	0.49	0.58
Graphene	82.65	17.35	-	-	-

X-Ray Photoemission Spectroscopy (XPS)

Material	% Composition / Atomic				
	C	O	Na	Cl	S
Graphite	97.83	1.78	-	0.17	0.22
Graphene	86.36	13.64	-	-	-

Elemental Analysis Method was conducted at The University of Otago, School of Chemistry, Campbell Microanalytical Laboratory, Dunedin, New Zealand.

Acid washed decolorizing charcoal (BDH Chemicals), 98-99% natural graphite (Hopkins and Williams), and synthetic graphite (Aldrich) were used for comparison.

The analytical method is based on the complete and instantaneous oxidation of the sample by “flash combustion” which converts all organic and inorganic substances into combustion products. The sample is held in a tin capsule and dropped into a vertical quartz tube, containing catalyst (tungstic oxide) and copper, which is maintained at a temperature of 1020°C. The helium carrier gas is temporarily enriched with pure oxygen as the sample is dropped into the tube. The sample and its container melt and the tin promotes a violent reaction. Under these favourable conditions, even thermally resistant substances are completely oxidized. Quantitative combustion is then achieved by passing the mixture of gases over a catalyst layer, then through copper to remove excess oxygen and reduce nitrogen oxides to nitrogen. The resulting mixture is directed to the chromatographic column where the components (carbon dioxide, water, sulfur dioxide and nitrogen) are separated and detected by a thermal conductivity detector which gives an output signal proportional to the concentration of the individual components of the mixture. The information is fed into a work station and the percentages calculated using the weight of sample.

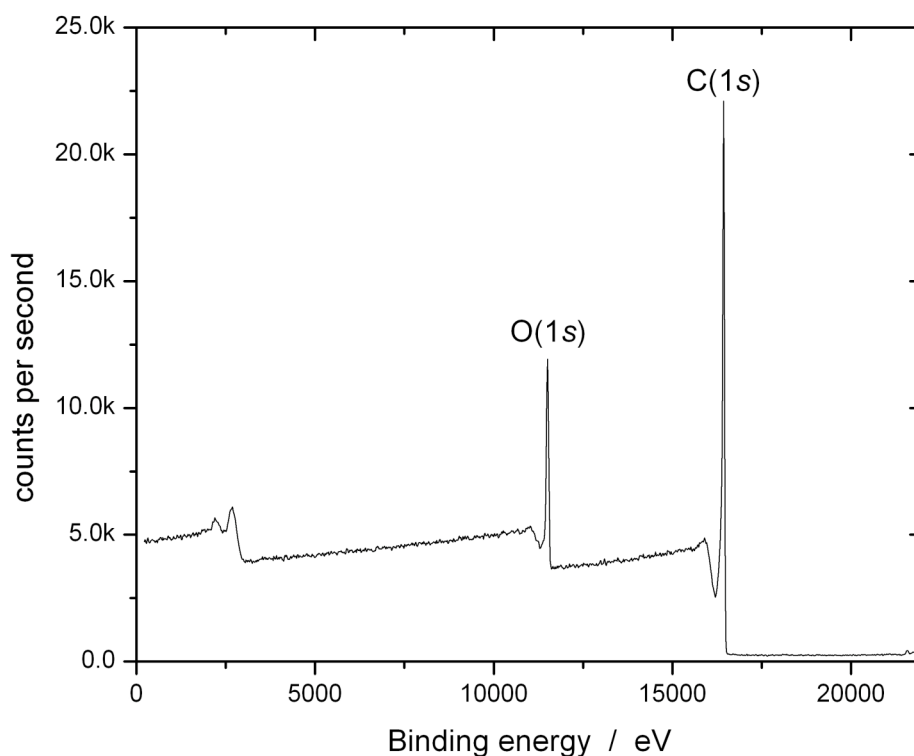


Figure S1. XPS spectra of the graphene sample.

The defective nature of the graphene synthesised gives rise to regions of the material where carbon is bound to oxygen, which is also apparent in natural graphite (Raman spectra showing it is defective to a certain degree). However, there is no evidence of a periodicity in this chemical bonding, as SAED patterns observed indicate bond lengths of a hexagonal arrangement of carbon atoms bound only to carbon atoms, agreeing with theoretical calculations. XPS spectra also shows that the graphene synthesised contains no trace elements after purification.

Raman Spectroscopy

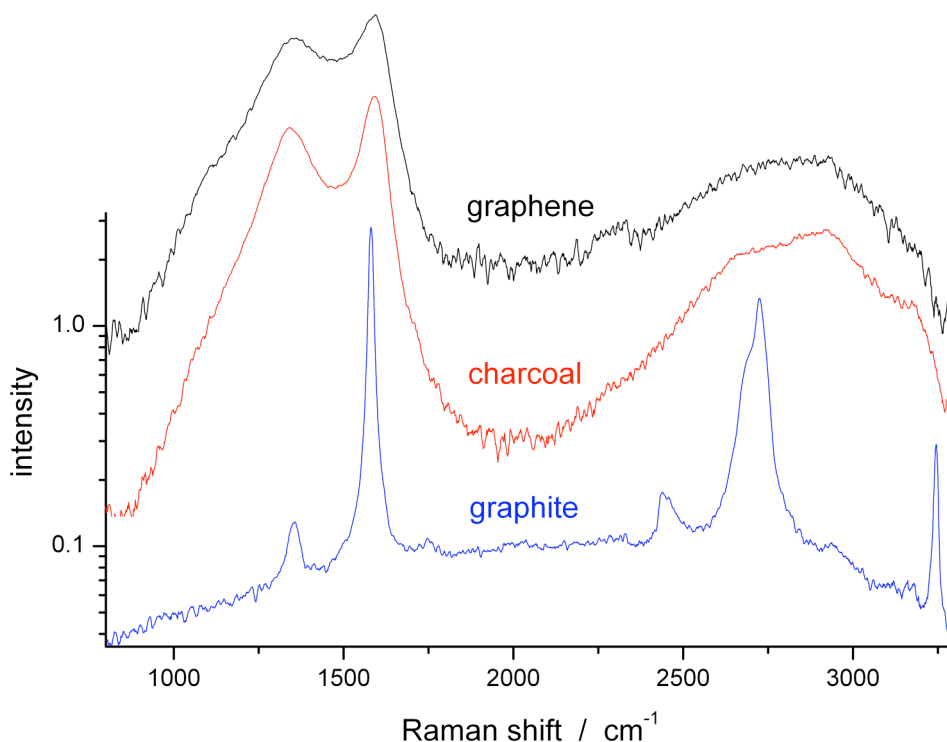


Figure S2. Raman spectra of carbonaceous materials (logarithmic vertical scale), (top) as-synthesized graphene, (centre) charcoal (bottom) natural graphite. All data obtained at 514 nm excitation and 4 cm⁻¹ resolution.

Raman spectroscopy has been regarded as being a rapid means of determining the precise nanostructures of carbonaceous materials (CNSs),[S1] despite the obvious limitation that the size of the laser focal point is typically microns. In addition, materials that are truly nanoscale inevitably have very high transmission of visible light. The combination of these factors can result in materials of very different nanostructure having inherently similar Raman spectra.[S2,S3]

Raman data of CNSs are often described in relation to that of graphite, in which so-called *G* (graphite) and *D* (defect) bands are present at ca. 1560 and 1360 cm⁻¹ respectively. For graphitic materials the intensity of the *G* band, due to the in-plane stretching motion between pairs of *sp*² carbon atoms, is very much greater than that of the *D* band, believed to be due to a double-resonance and enhanced by edge effects and dangling bonds of the *sp*² carbon sites. The rationale then follows that if $I_G \gg I_D$, then the number of defect sites must be very much lower than graphitic sites.

However, the number of edge sites rapidly increases as the lateral dimensions of the sheets decrease, hence populating the *D* band. In this respect, CNSs of different form, but similar aspect ratio, may display a similar value of I_G/I_D . The situation is further complicated by the fact that Raman peaks due to the carbon-carbon stretches in amorphous *sp*³ hybridized carbon also lie within this spectral window. Finally, graphene

sheets have an inherent tendency to overlay each other due to favourable π - π interactions, resulting in a high probability of illuminating numerous edge sites within any given focal point of μm dimensions, yielding $I_G \sim I_D$.

The observation of spectra having broad peaks of similar form across CNSs emphasises the need for further more discriminatory characterisation techniques such as atomic force microscopy and electron diffraction to confirm the presence of individual graphene sheets.

References:

- [S1]. Ferrari, C. A., Raman spectroscopy of graphene and graphite: Disorder, electron-phonon coupling, doping and nonadiabatic effects. *Solid State Commun.* **143**, 57-57 (2007).
- [S2]. Roy D. et al. Characterisation of carbon nano-onions using Raman spectroscopy, *Chem. Phys. Lett.* **373**, 52-56 (2003).
- [S3]. Kawakami M., Karato T., Takenaka T., Yokoyama S. Structure analysis of coke, wood charcoal and bamboo charcoal by raman spectroscopy and their reaction rate with CO_2 , *ISIJ Int.* **45**, 1027-1034 (2005).

Fourier Transform Infra-red Spectroscopy (FTIR)

Infra-red measurements were performed on the Nicolet Avatar 320 FT-IR and Thermo Nicolet Avatar 370 FT-IR spectrometers. The graphene sample was ground with KBr, and pressed into a thin disc.

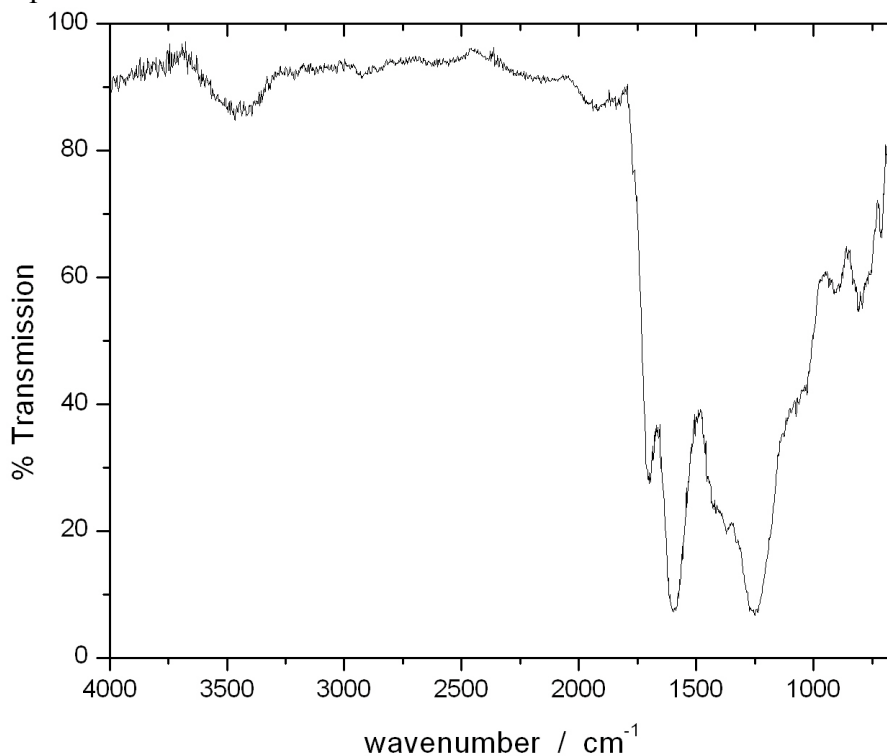


Figure S3. FTIR of graphene sample shows weak –OH stretching and C-O peaks.

The IR spectra taken shows that there is a small amount of water being absorbed after drying and preparation, with evidence of C-O bonding arising from either tightly bound water molecules or defective sites in the graphene.

Thermogravimetric Analysis (TGA)

Samples were ran in heat and hold mode at 10°C/min when purged with air, and 20°C/min when purged with nitrogen, to isothermal temperatures of 800°C and 60°C.

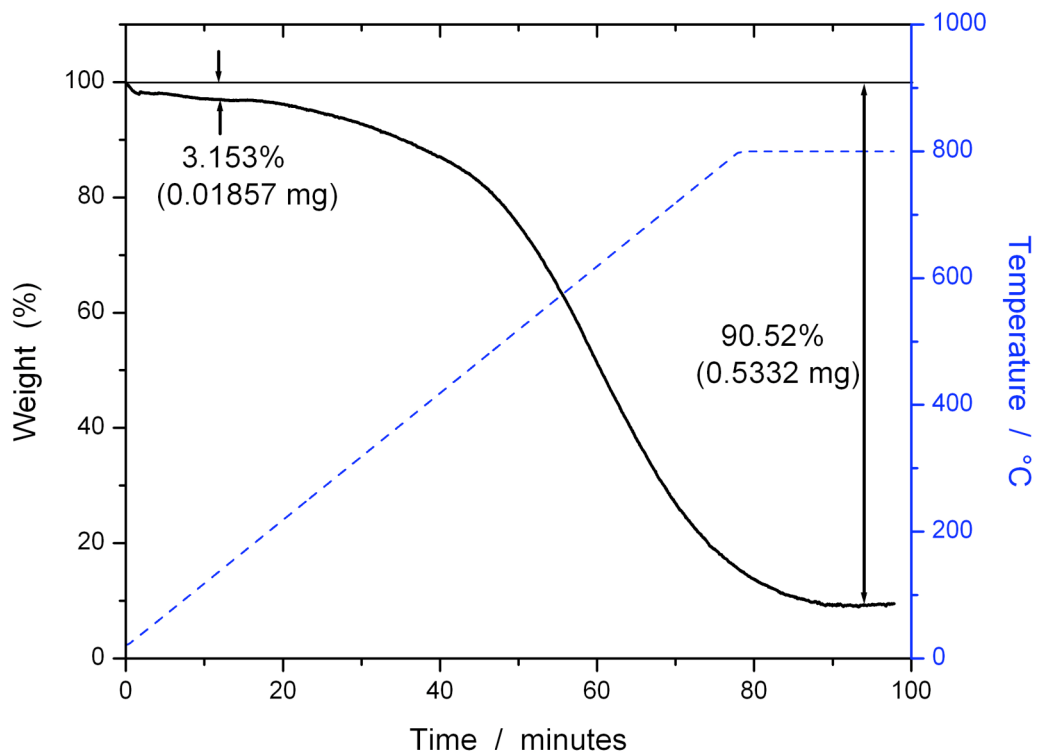


Figure S4. TGA of a pre-dried graphene sample heated under the flow of air to an isothermal temperature of 800°C.

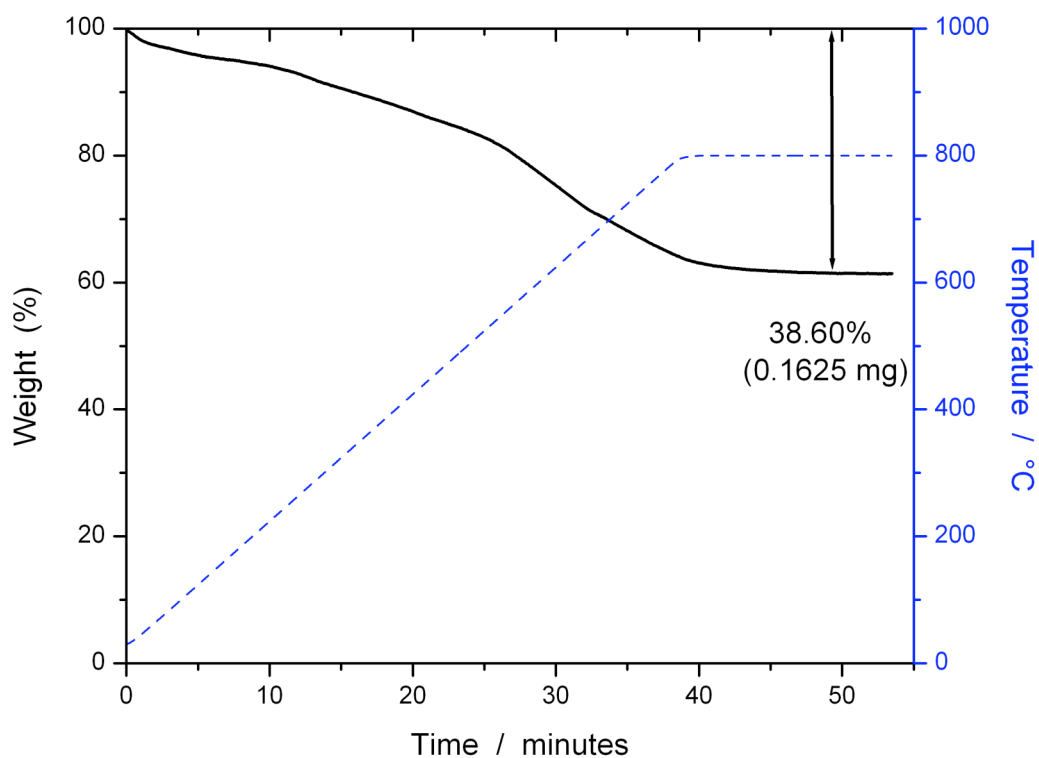


Figure S5. TGA of a pre-dried graphene sample heated under the flow of nitrogen to an isothermal temperature of 800°C.

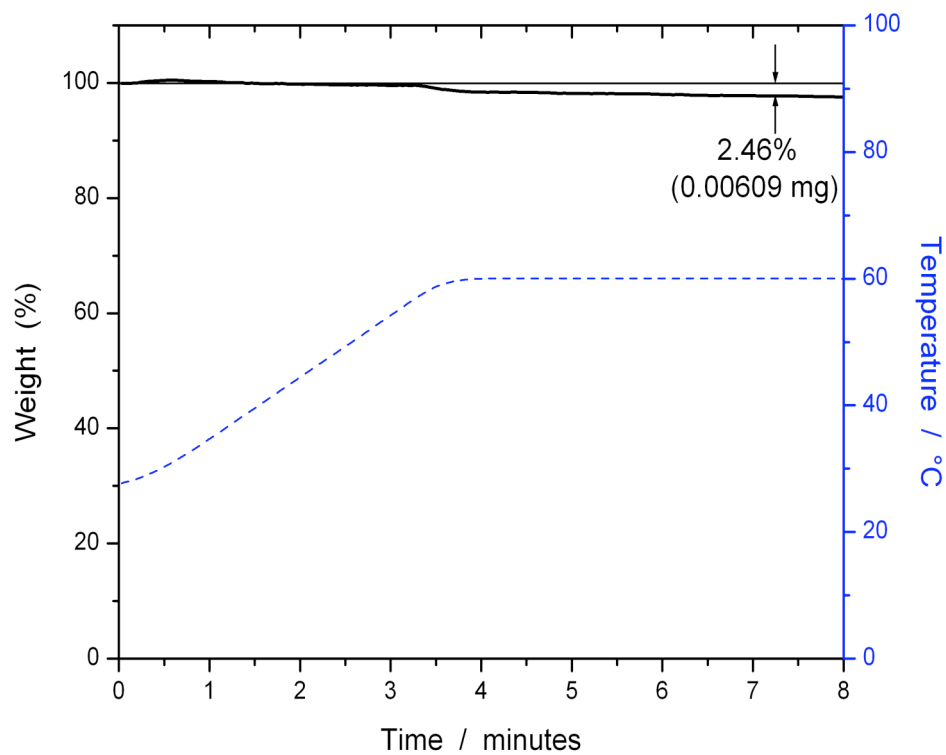


Figure S6. TGA of graphene sample heated under the flow of air to an isothermal temperature of 60°C.

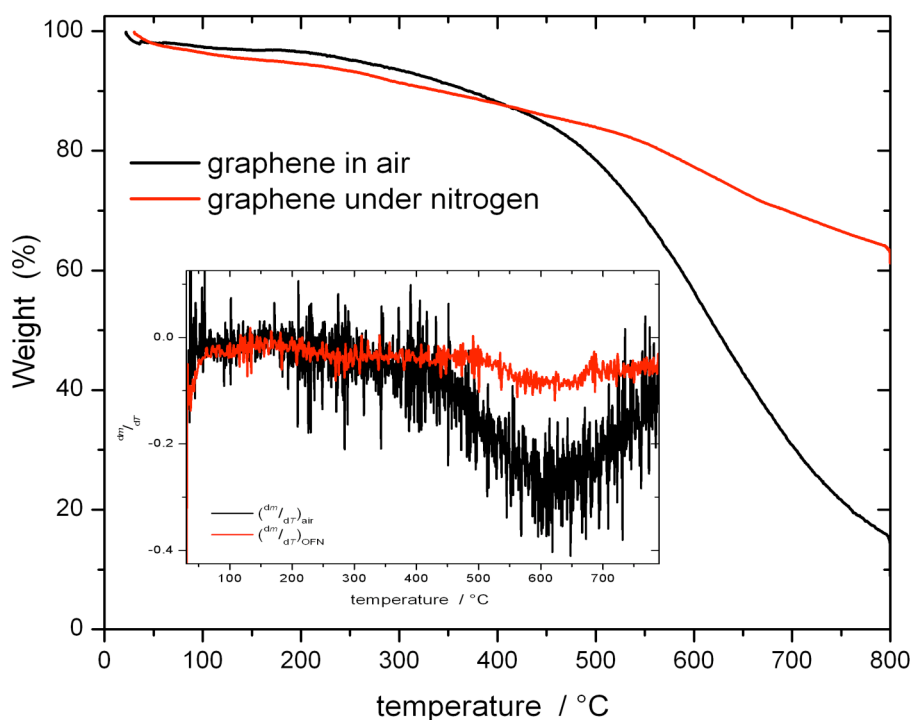


Figure S7. TGA of graphene heated under the flow of air (black) and nitrogen (red) to an isothermal temperature of 800°C. Inset: first derivative of TGA curve

The TGA of the pre-dried graphene sample conducted to 800°C under the purging of air shows some surface moisture being lost, followed by a thorough decomposition (pyrolysis) of the graphene material.

The TGA of the graphene sample conducted to 800°C under the purging of nitrogen shows some surface moisture being lost (ca. 7.5%), followed by some decomposition of the graphene material.

The TGA of the graphene sample conducted at 60°C under the purging of nitrogen shows some surface moisture being lost (ca. 2.5%).

The TGA responses of samples heated under both air and nitrogen follow a common path to around 400°C - particularly prevalent in the differential plot - beyond which the air-heated sample rapidly decomposes via combustion, whilst under nitrogen, only a partial decomposition is observed (possibly as a result of residual oxygen). The % weight loss at the point that the two curves diverge is ca. 13%, suggesting a residual value for bound water that includes strongly-bound molecules.

TGA-MS Supplementary Information

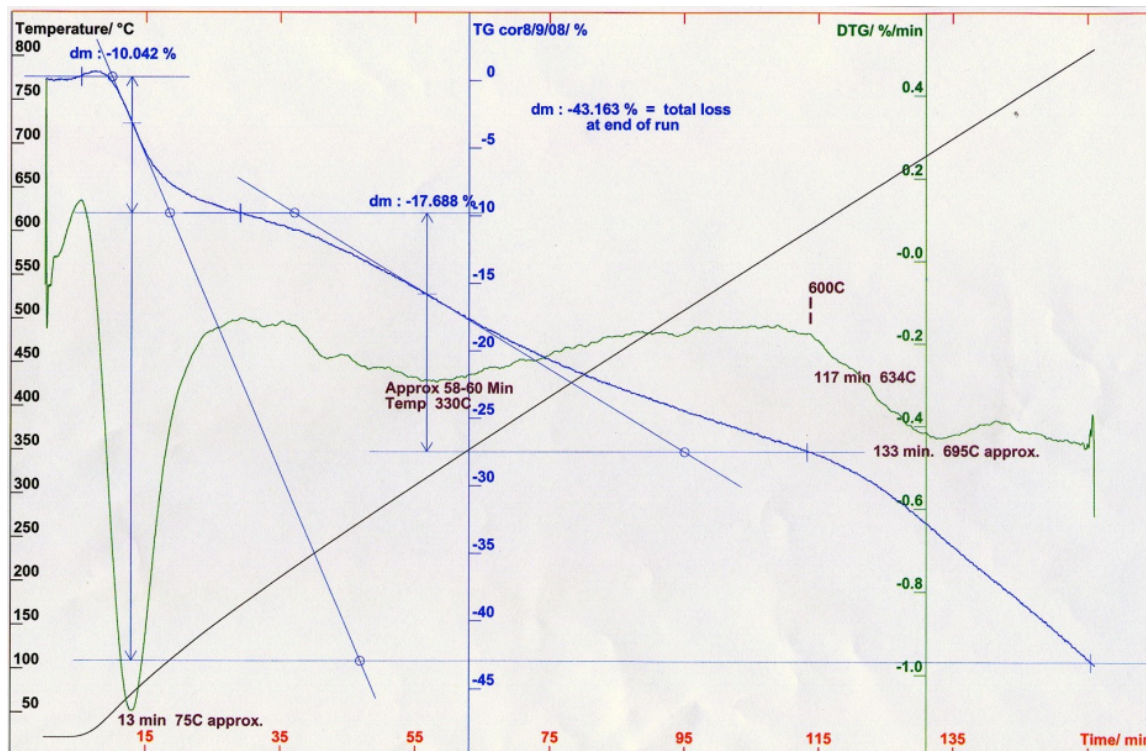


Figure S8. TGA data showing the: (blue) mass loss, (green) 1st differential of the mass loss, and (black) temperature all as a function of time.

The data (Fig. S8) shows an initial mass loss of ca. 10% up to ca. 150°C indicating water loss, followed by slight decomposition of the defective graphene to form CO₂ at ca. 330°C. Beyond 600°C the sample undergoes pyrolysis, liberating considerable quantities of CO and CO₂.

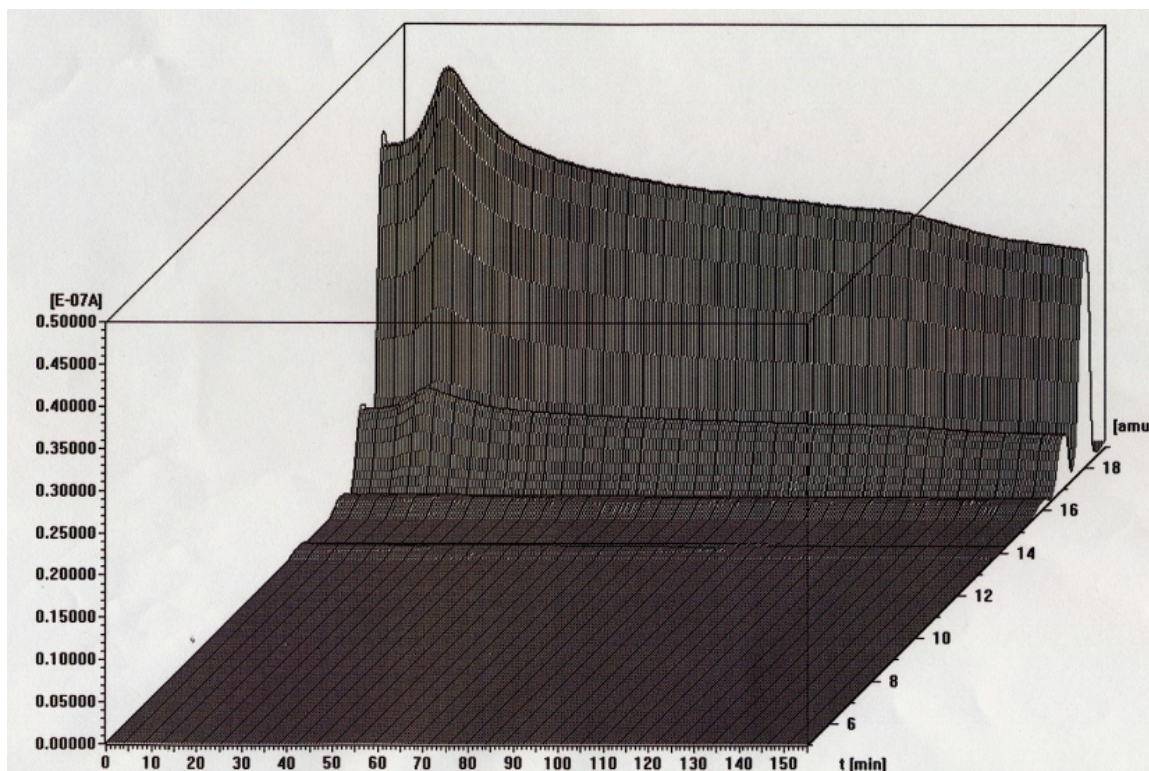


Figure S9. Mass spectrometry (MS) cycles obtained over the duration of heating emphasising 18 amu fragments (water).

The MS spectra for water (Fig. S9) showed that there was an increase in the 18 amu peak, with the a maximum amount of water being given off after around 13 minutes at a temperature of around 75°C, in agreement with the peak value of mass loss due to water in the TGA data. The evolution of water then steadily decreases over time.

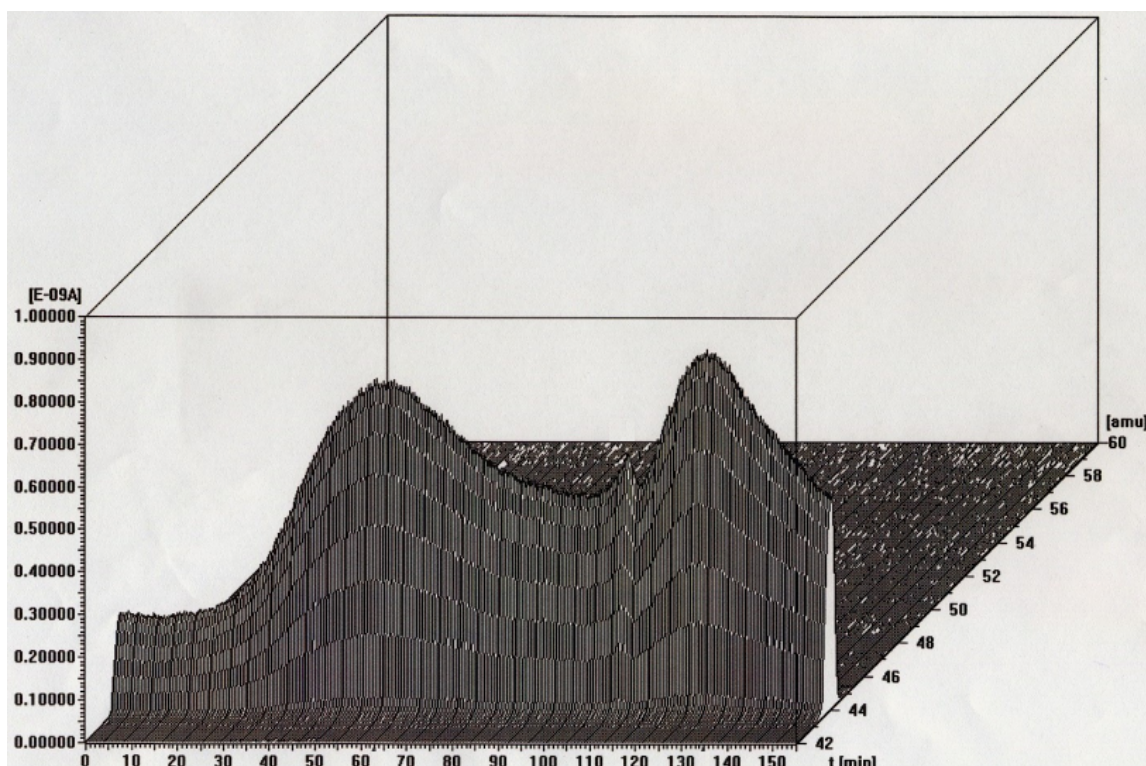


Figure S10. Mass spectrometry cycles obtained over the duration of heating showing 44 amu fragments (carbon dioxide).

Carbon dioxide was detected after around 60 minutes (corresponding to $T \sim 330^{\circ}\text{C}$), with small traces of CO_2 detected at ca. 150°C , Fig. (S10). Carbon dioxide was also observed during pyrolysis (ca. 120 minutes).

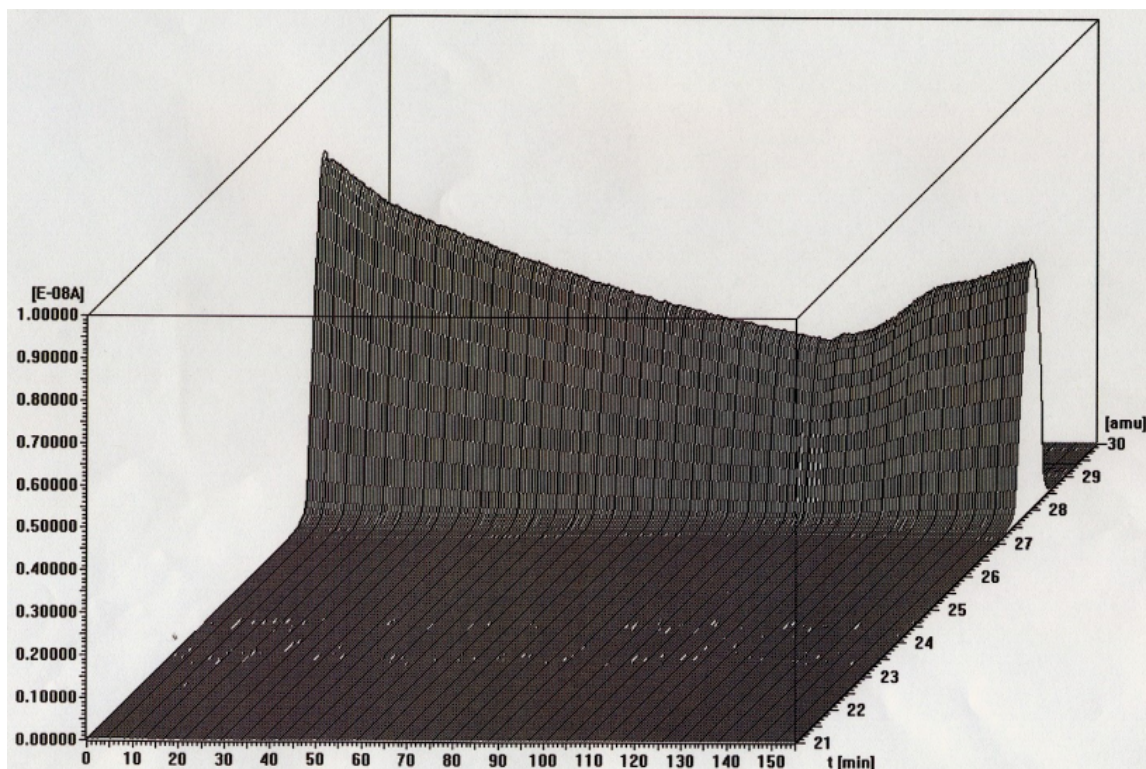


Figure S11. Mass spectrometry cycles obtained over the duration of heating showing 28 amu fragments (nitrogen and carbon monoxide).

Both nitrogen and carbon monoxide (CO) have molecular mass values of 28 amu, complicating the definitive detection of CO, (Fig. S11). However, as argon was used to purge the system, any residual nitrogen inside of the chamber was diluted (pumped through) over time. The effect of this is the gradually decreasing signal at 28 amu over the first 115 minutes (also suggesting that no CO is evolved over this time due to the continuous signal loss). At around 115 minutes ($T \sim 600^{\circ}\text{C}$) the 28 amu signal dramatically increases, indicating that carbon monoxide is produced during sample pyrolysis.

Experimental Conditions

The thermal analyser is a SETARAM (made in France, Caluire) TG/DSC Mle Setsys 16/18. It is composed of a micro balance with taut torsion strip suspension. The mass range used for the run was ± 20 mg, with a theoretical resolution of $0.04\ \mu\text{g}$. We used a TG/DSC plate transducer with TC Pt-Pt/Rh 90-10% (S type). The furnace (20°C to 1500°C) is gas-tight and was swept with Argon (BOC 062 $\text{O}_2 < 10$ ppm) for 1.5 hours with approximately 4 times the internal volume, before the test. The analysis of data was done with the Setaram Setsoft software version 1.53 (1999).

The evolved gas analysis was carried out with a BALZERS quadrupole ThermoStar model BK M26 266 T3. The mass-range is 2 to 300 amu, with ionisation by electron impact. The furnace-MS interface is a silica capillary maintained heated to 200°C . The scanning method used in the runs was cyclic (5 to 60 amu repeated every 30 seconds). The start and finish of MS data acquisition was synchronized with start and end of the

heating ramp (20°C to 800°C at 5°C/min). MS data was analysed using Balzers Quadstar 422 software version 6.02 1999.

TGA-FTIR

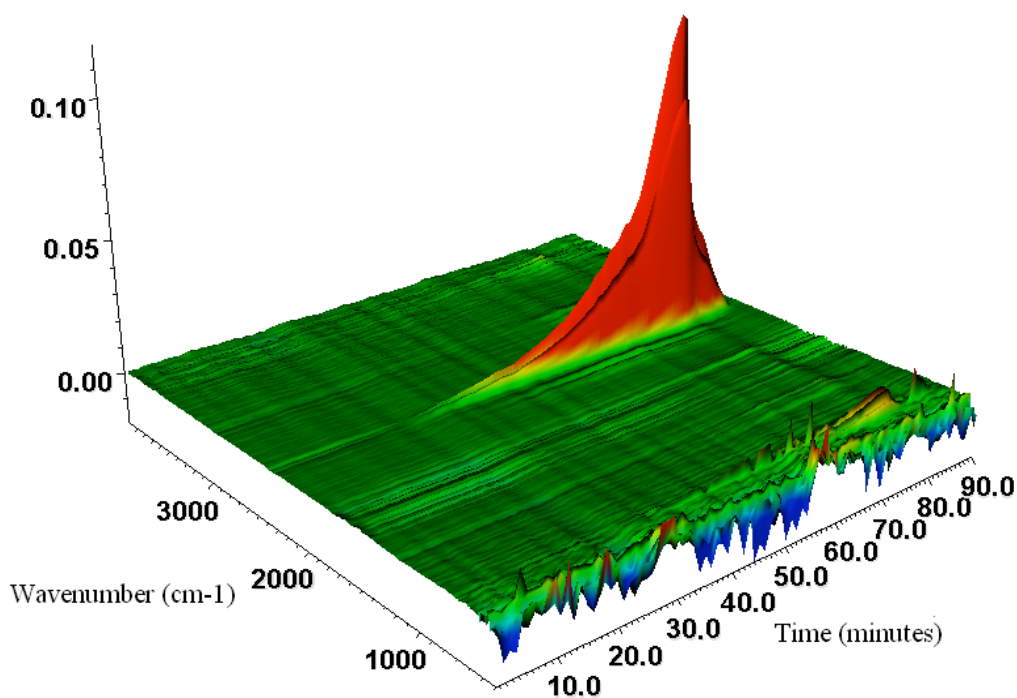


Figure S12. Sample dried at 150°C under vacuum for 24h.

Analysis was performed using a TA Instruments TGA 2050 connected to a 5700 Nicolet IR using a TGA-FTIR interface unit. A DTGS detector was used with a scan range of 400-4000 cm⁻¹ with a resolution of 4 cm⁻¹, with the sample being purged under nitrogen gas. Infra-red spectra were recorded every minute for 90 minutes during a ramped heating programme of 10°C/min, (Fig. S12).

Preliminary analyses indicated that samples that were not thoroughly dried prior to analysis contained significant quantities of water. Once dried under vacuum at 150°C, all of the water was removed from the sample, with CO₂ evolution beginning around 340°C. None of the sampled-TGA data supports the evolution of CO or CO₂ at temperatures significantly below 340°C.

Mass spectrometry (MS)

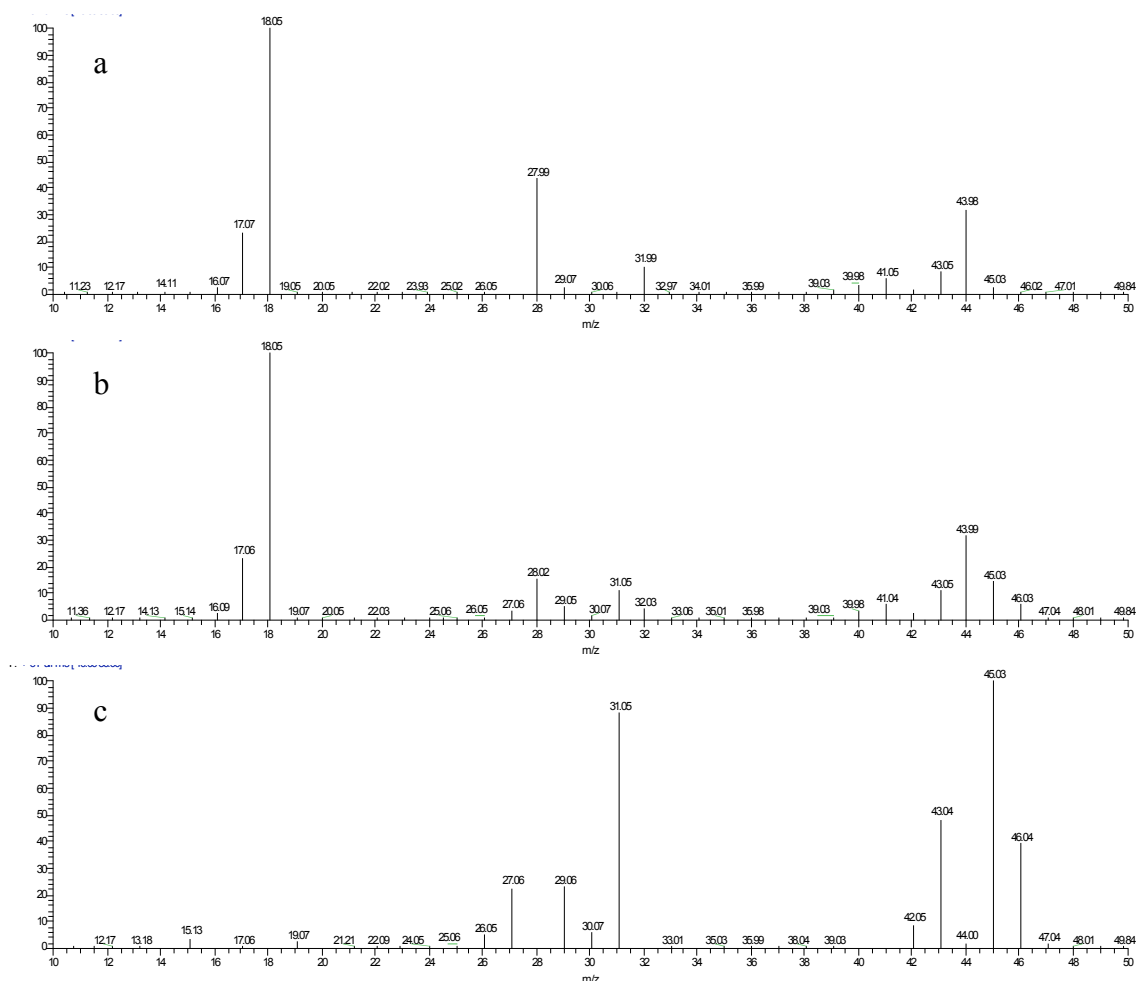


Figure S13. Fragments obtained by electron ionization mass spectroscopy of a) background (air) b) a graphene sample washed with copious amounts of ethanol during purification and c) a subtracted spectra of the background and graphene sample, showing ethanol present.

Samples (approx. 1 mg) were analyzed by direct insertion probe electron impact ionization (EI⁺) mass spectrometry, using a Thermo DSQ II mass spectrometer (Thermo Fisher Scientific Inc., Waltham, MA). The mass spectrometer scanned from m/z 10 to m/z 50 in 0.33 seconds. The direct insertion probe was maintained at 50°C for 1 minute, then heated ballistically to 200°C and held at that temperature for 90 seconds. The ion source was maintained at a temperature of 150°C and all sample cups were pre-heated to 200°C in vacuo prior to sample loading, or acquisition of background spectra. Control analyses were performed using empty sample cups, and the data obtained were used to provide background subtraction for carbon sample spectra. Background subtracted spectra were searched against the Wiley 7 and NIST 98 mass spectral libraries to provide identification of the desorbed analytes.

From the data obtained after subtracting the background, water and molecular oxygen do not appear to be present. Rather, fragments of ethanol are exemplified, remaining after washing (i.e. the sample was wet with ethanol). However, the absence of water and

molecular oxygen fragments in the subtracted spectra can also suggest that the amount of water and molecular oxygen in the sample are comparable to that in the atmosphere.

The high abundance of water and molecular oxygen in air make it difficult to distinguish their presence in the graphene sample, as the primary indication of their presence would be by observation of an increase in their fragment signals. The presence of water and molecular oxygen in the graphene sample could also result in a blank spectrum upon subtraction of the background (air) spectrum, as comparable amounts could be present in both air and the sample in air.

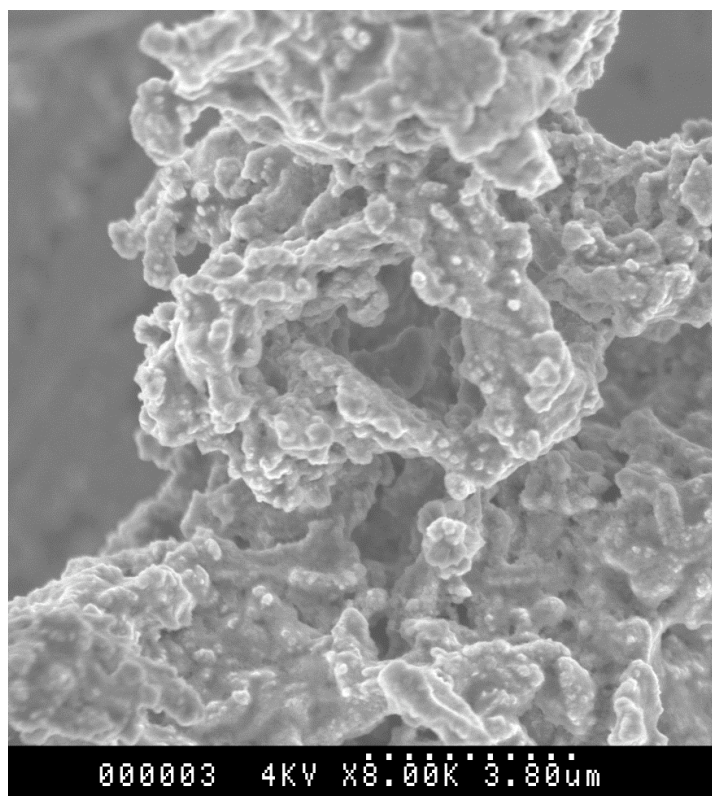
SEM Supplementary data

Figure S14. SEM image of the solvothermal product (graphene precursor). The porous nature of the material is clearly evident, with cavities of 1-3 μm in diameter, thus facilitating the high storage capacity for ethanol (of up to ca. 30% by weight).

AFM Supplementary data

Fig. 4 shown in the article is not unique; below are two more examples showing the topography images of various graphite sheets on top of each other. Height profiles are indicated by white arrows. These images have been levelled by 2nd or 3rd - order plane subtraction and no other data manipulation was done on these images.

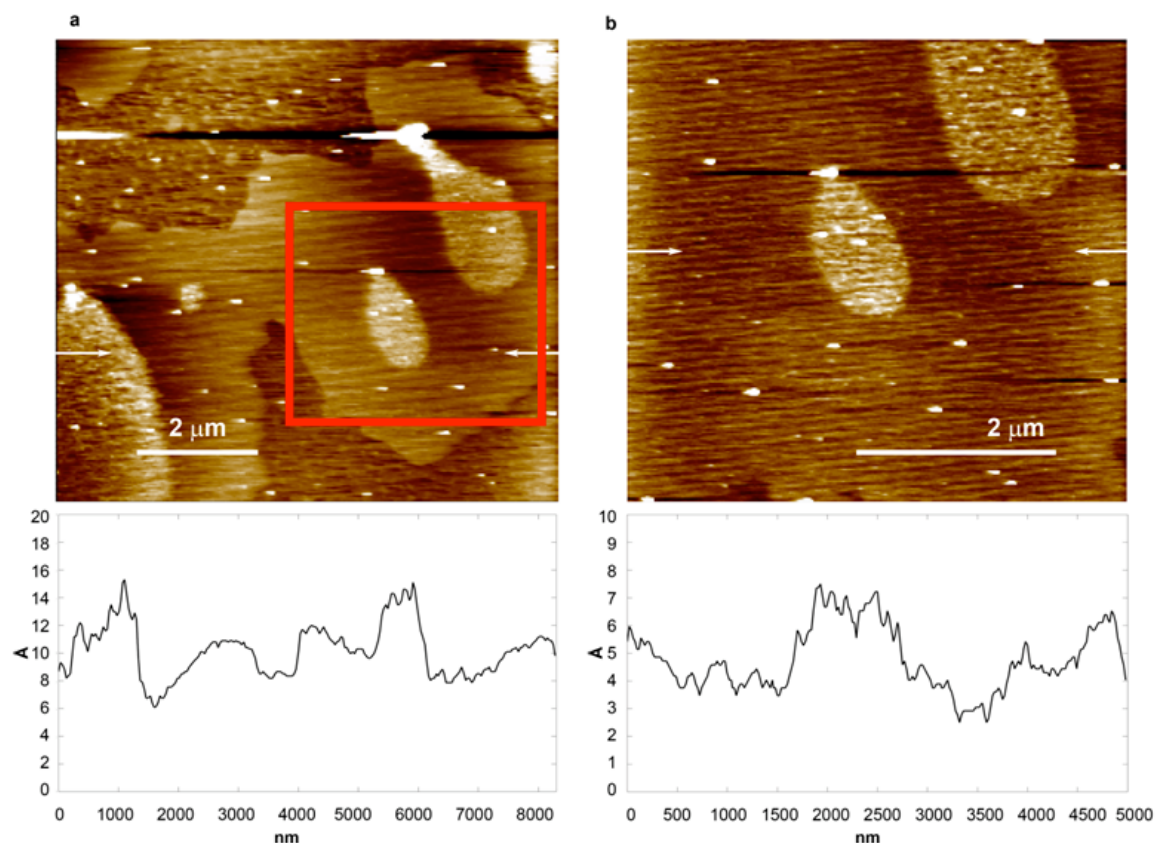


Figure S15. a) Top: AFM topography image (levelled by a 2nd order plane subtraction) of a dried ethanol suspension of graphene on mica. Bottom: Height profile obtained by taking a horizontal cross-section as indicated by the white arrows on the top image. b) A close-up (zoom) topography image of the area indicated by a red rectangle in red on the left-hand image.

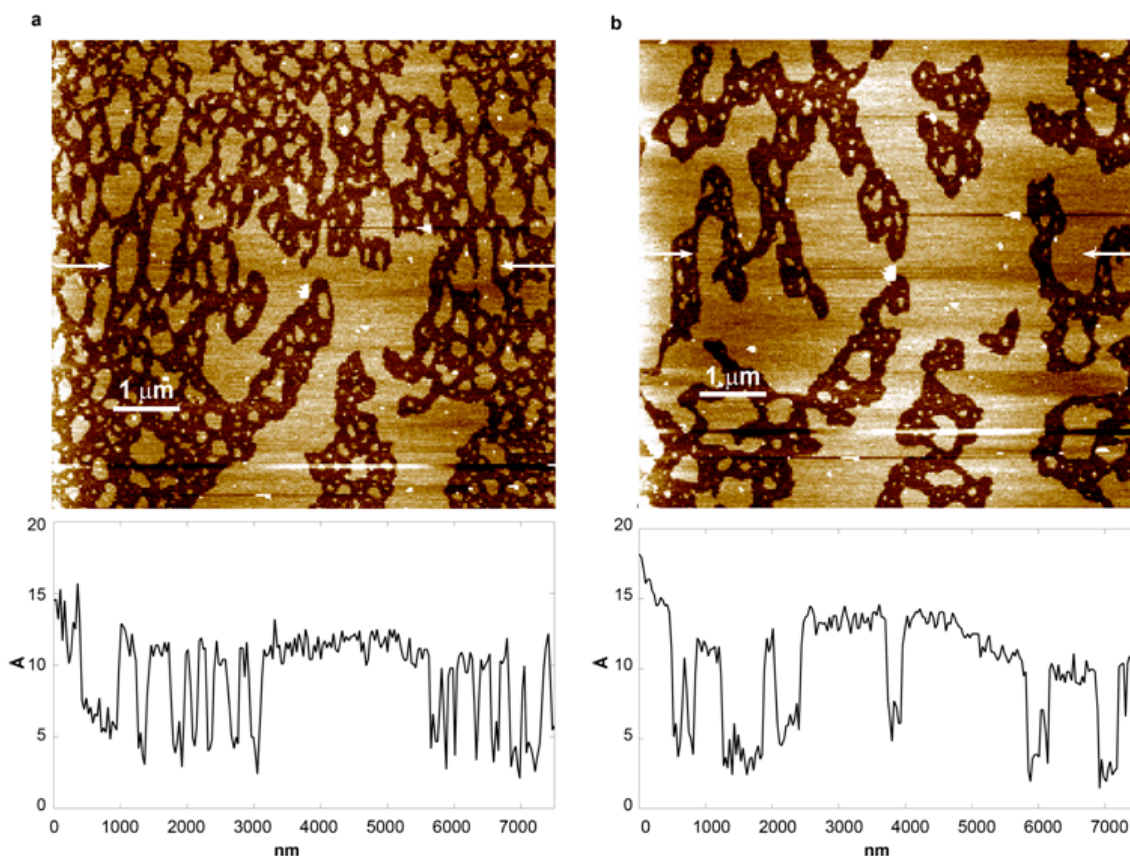


Figure S16. a and b) Two different areas showing graphene double layers. Top: AFM topography images (levelled by a 3rd order plane subtraction) of a dried ethanol suspension of graphene on mica. Bottom: Height profile obtained by taking a horizontal cross-section as indicated by the white arrows on the top images.

Note: Plane subtraction is applied to correct for the non-linearity of the piezo-AFM scanner but a sloping baseline may still remain. A residual slope in the baseline may still be detected and combined with tip-convolution effects may make some of the steps in the above images appear to be at little less or more than 4-5 Å (single sheets in Fig. S15) or 7-9 Å (double sheets in Fig. S16).

Bulk Conductivity

The conductivity of a bulk sample of graphene was taken by pressing the graphene powder into a disc using a 15 mm (diameter) dye under a hydraulic press and measuring the resistance between two points on the sample. The conductivity was calculated using the equation:

$$R = \frac{\rho L}{A} \quad \dots 1$$

where R is resistance, ρ is resistivity, A is the cross-sectional area of the sample in contact with the electrodes, and L is the distance between the electrodes, with the conductivity being the inverse of resistivity:

$$\sigma = \frac{1}{\rho} \quad \dots 2$$

The conductivity of natural graphite was taken for comparison. The conductivity was measured both across the surface of the pressed discs, and between the two sides of the discs. The results are summarised below.

Sample	Conductivity (Sm^{-1})	
	Across Surface	Between Surfaces
Graphite	5.0×10^3	11.4×10^3
Graphene	0.067	0.017
Charcoal ^a	10^{-5} - 10^{-8}	

[a] A.R. Coutinho, J.D. Rocha, C.A. Luengo. "Preparing and characterizing biocarbon electrodes", Fuel Processing Technology, **67** 93–102 (2000).

The graphene conductivity lies almost half way between graphite and charcoal.