

Electronic Supporting Information

Formation and Chemistry of Carboxylic Anhydrides at the Graphene Edge

Martin Rosillo-Lopez,^a Tai Jung Lee,^a Malika Bella,^b Martin Hart^a and Christoph G. Salzmänn^{a,*}

^a University College London, Department of Chemistry, 20 Gordon Street, WC1H 0AJ London, UK.

E-mail: c.salzmänn@ucl.ac.uk

^b Durham University, Department of Chemistry, South Road, Durham DH1 3LE, UK

Table of contents

1	Sample characterisation	2
1.1	Optical absorbance spectroscopy	2
1.2	X-Ray photoelectron spectroscopy (XPS)	2
1.3	Atomic force microscopy (AFM)	2
1.4	Solid state NMR spectroscopy	2
1.5	Raman spectroscopy	2
1.6	Attenuated total reflectance infrared spectroscopy (ATR-IR)	2
1.7	Temperature programmed desorption with mass spectrometry (TPD-MS)	3
1.8	Zeta-potential measurements	3
1.9	Transmission electron microscopy	3
2	Preparation of carboxylated graphene nanoflakes (cx-GNFs)	3
2.1	Optimal reaction conditions for the preparation of cx-GNFs	3
2.2	Large-scale preparation of cx-GNFs	4
2.3	Synthesis of cx-GNFs from Elicarb MWCNTs	4
3	Preparation of graphene oxide (GO)	5
4	Chemical functionalisation of cx-GNFs	5
4.1	Synthesis of <i>eth</i> -GNF and <i>cys</i> -GNF	5
4.2	Synthesis of <i>Al</i> -GNFs	6
4.3	FT-IR spectra of <i>eth</i> -GNFs and <i>cys</i> -GNFs	6
4.4	XPS spectra of <i>eth</i> -GNFs, <i>cys</i> -GNFs and <i>Al</i> -GNFs	6
5	TPD-MS measurements	7
5.1	Detailed analysis of the H ₂ O and CO ₂ desorption from cx-GNFs	7
5.2	Thermal gas desorption patterns of GO	8
6	Transmission electron microscopy (TEM) measurements	8
7	Stability of anhydride-containing GNFs (an-GNFs) in water and air	8
8	References	9

1 Sample characterisation

1.1 Optical absorbance spectroscopy

Optical absorbance spectra of aqueous dispersions were recorded on a Perkin Elmer Lambda 900 spectrometer using 1 cm quartz cuvettes and a scan rate of 120 nm min⁻¹.

1.2 X-Ray photoelectron spectroscopy (XPS)

All XPS measurements were carried out on a Thermo Scientific K-Alpha XPS machine with a monochromated Al K_α source ($E=1486.6$ eV), a double focusing 180 degree hemisphere analyser of ~125 mm radius and detected with a 18 channel position sensitive detector. A dual beam flood gun (electrons and argon ions) was used to compensate for charge accumulation on the measured surfaces. All survey scans were scanned 3 times with a resolution of 1 eV, 400 μm spot size and 50 ms dwell time. All elemental regions were scanned 10 times with a resolution of 0.1 eV, 400 μm spot size and 50 ms dwell time. The spectra were analysed with the CasaXPS software.

1.3 Atomic force microscopy (AFM)

For AFM analysis, aqueous *cx*-GNF dispersions (~0.1 mg mL⁻¹) were dropped onto freshly cleaved 'highly oriented pyrolytic graphite' (HOPG) using a Laurell Technologies WS-650 spin-coater (2000 rpm). A Digital Instruments Multimode Nanoscope scanning probe microscope with an IV Nanoscope controller manufactured by Bruker was used for AFM measurement in the tapping mode using the 'E' scanner. For labelling chemically functionalised GNFs with Au nanoparticles, one drop of 5 nm Au nanoparticles dispersed in 0.1 mM phosphate buffered saline solution was spin coated at 2000 rpm for 2 min onto a freshly cleaved HOPG substrate as described previously. The GNFs (one drop, ~0.1 mg mL⁻¹) were then spin coated onto the same substrate in the same way as before.

1.4 Solid state NMR spectroscopy

A Bruker Avance 300 spectrometer with 7.05 T wide-bore magnet at ambient probe temperature was used to perform all solid-state ¹³C measurements. High-resolution ¹³C solid-state NMR spectra were recorded at 75.5 MHz with a Bruker 4 mm double-resonance magic-angle spinning (MAS) probe using high-power proton decoupling (HPDEC). The operating conditions were ¹³C 90°C pulse with a 3.7 μs delay; recycle delay of 120 s with 908 transients. The *cx*-GNFs and graphene oxide were packed into zirconia rotors of 4 mm external diameter and spun at 12 kHz MAS frequency with a stability greater than ±3 Hz. The ¹³C chemical shifts are reported with respect to tetramethylsilane (TMS) which was calibrated against an aqueous solution of 4,4-dimethyl-4-silapentane-1-sulfonic acid (DSS, 0 ppm), and glycine (176.46 ppm) respectively.

1.5 Raman spectroscopy

All Raman measurements were carried out on a Renishaw Ramascope using a 633 nm laser, 50-fold magnification objectives, scan times of 20 seconds and accumulation of 4.

1.6 Attenuated total reflectance infrared spectroscopy (ATR-IR)

FT-IR spectra were collected on a Bruker Tensor 27 FTIR spectrometer using the attenuated total reflectance infrared spectroscopy mode (ATR-IR) fitted with a room temperature DLaTGS detector at 4 cm⁻¹ resolution and a diamond crystal as the internal reflection element. A background spectrum was allowed to run for 256 scans before recording each sample measurement which were then recorded for the same length of time.

1.7 Temperature programmed desorption with mass spectrometry (TPD-MS)

2.5 mg of the carbon nanomaterials were carbonised by heating from room temperature to 900°C at 10°C min⁻¹ under high-vacuum conditions with a base pressure of $\sim 1.5 \times 10^{-5}$ mbar using a Carbolite MTF 1200 horizontal tube furnace. The total pressure increases resulting from desorbing gas were monitored *in-situ* as a function of temperature using a PTR225 cold cathode pressure gauge from Leybold. The nature of the gaseous species were analysed with a HAL RC 201 mass spectrometer from Hiden Analytical using a Faraday Cup as the detector by scanning along the 1 to 200 a.m.u mass range every 5°C from room temperature to 900°C. Once the sample reached 900°C the carbonised material was cooled quickly back to room temperature under vacuum before leaking to the atmosphere and recovering the samples.

1.8 Zeta-potential measurements

All zeta potential measurements were carried out on a Malvern Zetasizer Nano (ZEN3600) machine using disposable DTS 1060C plastic cuvettes.

1.9 Transmission electron microscopy

A JEOL JEM 2100 transmission electron microscope (TEM) with a Lanthanum hexaboride electron gun with 200 kV electron energy along with a Gatan Orius camera was used to perform all TEM measurements. Prior to TEM imaging, samples were drop coated (2 drops, conc. ≈ 0.05 mg / mL) onto a copper grid coated with lacy carbon.

2 Preparation of carboxylated graphene nanoflakes (cx-GNFs)

2.1 Optimal reaction conditions for the preparation of cx-GNFs

C150P Baytube multi-wall carbon nanotubes (MWCNTs) prepared using a CVD process by Bayer Materials Science (3 to 15 walls of 5 to 20 nm outer diameter, 2 to 6 nm inner diameter, 1 to 10 μ m in lengths and free of amorphous carbon) were used as the starting material for the preparation of the cx-GNFs. To optimise the yield and to minimise the basal plane oxidation of the cx-GNFs the effects of reaction time and oxidation medium were investigated. Specifically, in a set of experiments, 10 mg of the MWCNTs were ultrasonicated in 5 mL of either a 3:1 or a 1:1 vol% mixture of conc. sulfuric acid (95-97% w/w) and conc. nitric acid (70% w/w) for 30 minutes. The reaction mixtures were then heated at 100°C for variable amounts of time, left to cool, diluted three-fold with distilled water and filtered through a 0.2 μ m track-edged polycarbonate membrane. The optimal reaction time and conditions were determined by measuring the absorbance of the filtrates at 500 nm (*cf.* Fig. S1). Two hours reaction time in the 3:1 vol% acid mixture were identified as the optimal conditions.

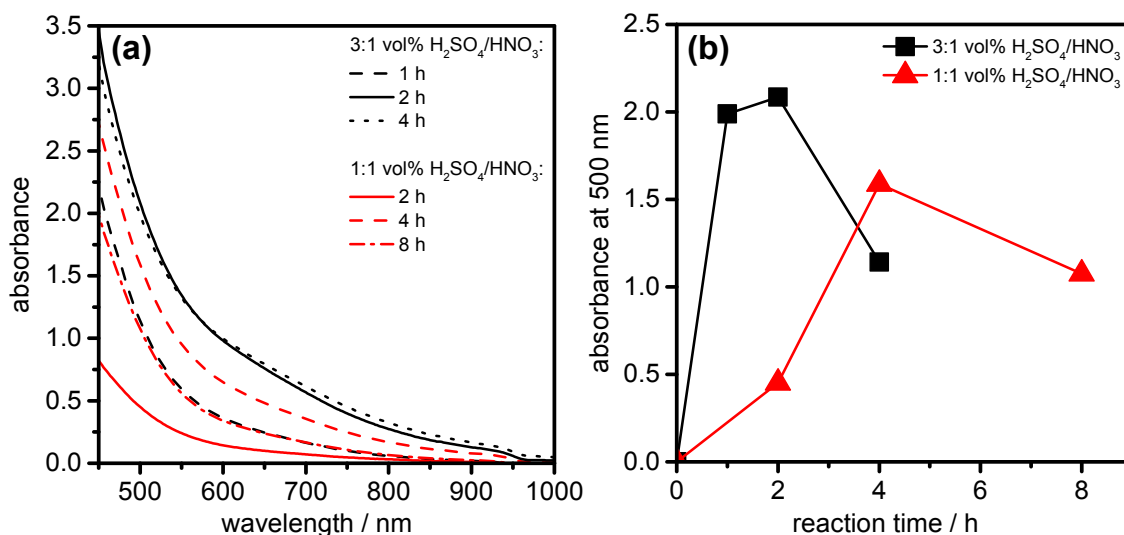


Figure S1 (a) Optical absorbance spectra of the filtered reaction mixtures after oxidation in (i) 3:1 H_2SO_4/HNO_3 after 1 hour (black dotted), 2 hours (black solid) and 4 hours (black dashed) and (ii) 1:1 $H_2SO_4:HNO_3$ after 2 hours (red solid), 4 hours (red dashed) and 8 hours (red dot-dashed). (b) Absorbance values of the spectra in (a) at 500 nm.

2.2 Large-scale preparation of *cx*-GNFs

Hazard Warning. Concentrated sulfuric acid and nitric acid are corrosive and highly oxidizing. Potassium hydroxide is highly corrosive and hygroscopic.

For a large scale preparation of *cx*-GNFs, 500 mg of the MWCNTs were ultrasonicated in 250 mL of a 3:1 vol% mixture of conc. sulfuric acid (95-97% w/w) and conc. nitric acid (70% w/w) for 30 minutes. The reaction mixture was heated at 100°C for two hours, left to cool and then diluted three-fold with distilled water. The resulting dispersion was filtered through a 0.2 μm track-edged polycarbonate membrane, the black residue on the membrane was discarded and the brown-black filtrate was neutralised by addition of KOH pellets with external ice bath cooling. After neutralisation, a white salt precipitate was removed by filtration (*cf.* Fig. 1(b)) and the black filtrate was concentrated *in vacuo*. The dispersion was first dialyzed against 1 M formic acid and then against high-purity *Milli-Q* water using SpectraPor 6 dialysis membranes (MWCO 3.5 kDa). The progress of the dialysis was monitored with a Mettler Toledo conductivity meter using a Mettler Toledo LE703 conductivity sensor. The resulting dispersion was passed over a cation exchange resin (Amberlite IR120, Sigma-Aldrich) and then freeze dried to give ~80 mg of brown-black *cx*-GNFs.

2.3 Synthesis of *cx*-GNFs from Elicarb MWCNTs

In addition to using C150P Baytubes, we show that *cx*-GNFs can also be synthesised from Elicarb CVD MWCNTs (Thomas Swan Ltd). The XPS data below shows the survey and C1s spectra of *cx*-GNFs derived from Elicarb material using the same procedure detailed above. In the following, we will, however, use the *cx*-GNF material derived from the Baytubes.

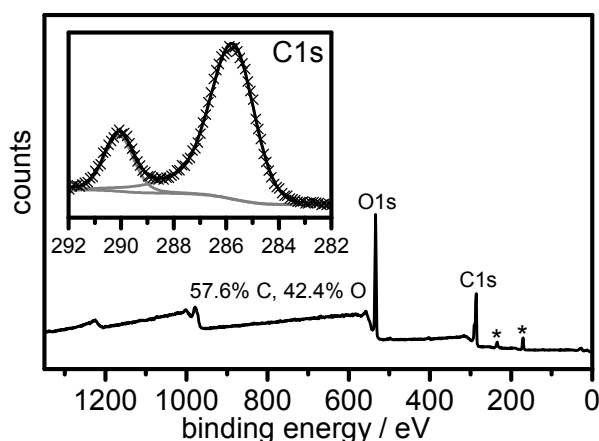


Figure S2. XPS survey spectrum and C1s region of *cx*-GNFs synthesised from Elicarb MWCNTs. Asterisks indicate silicon dioxide contaminations arising from etched glassware.

3 Preparation of graphene oxide (GO)

Hazard Warning. Potassium permanganate and sulfuric acid form a highly oxidizing mixture which is potentially explosive in the presence of organic compounds such as acetone or ethanol. Hydrogen peroxide acts as both a strong oxidizing and reducing agent. Exact control of temperature is paramount for the safe preparation of GO.

For comparison of our *cx*-GNFs with another oxidised carbon nanomaterial GO samples were prepared following a somewhat modified procedure by Chen *et al.*^{1, 2} Graphite flakes (1.00 g, > 100 mesh, Sigma-Aldrich) and concentrated sulfuric acid (25 mL, > 95 % w/w) were combined and stirred at 0°C. Under vigorous agitation, potassium permanganate (3 g) was added slowly so that the temperature of the reaction mixture never exceeded 20°C. After this, the reaction mixture was heated at 40°C for 30 minutes. Distilled water (50 mL) was then added and the solution stirred for a further 15 minutes at 95°C. The brown mixture was then diluted by addition of 175 mL of water followed by dropwise addition of 10 mL of 30% v/v hydrogen peroxide. The yellow-green mixture was filtered through a Whatman paper membrane, washed with 150 mL of 10% aqueous HCl and allowed to dry. The dry powder was dispersed in 200 mL of distilled water and dialyzed against a pre-treated standard grade, regenerated cellulose dialysis membrane (Spectrum Laboratories, MWCO 3.5 kDa). After dialysis, the graphite oxide was exfoliated *via* ultrasonication for 90 minutes. The dispersion was then centrifuged at 3000 rpm for 40 minutes and decanted to isolate the exfoliated GO. The GO was then ultrasonicated once more for 30 minutes and the dispersion filtered through glass wool. The filtrate was collected and passed over a cation exchange resin (Amberlite IR120, Sigma-Aldrich), concentrated and then dried to give ~1 g of a brown powder.

4 Chemical functionalisation of *cx*-GNFs

4.1 Synthesis of *eth*-GNF and *cys*-GNF

20 g of 5 wt % ethylenediamine or cysteamine in deionised water were added to 5 mg of *cx*-GNFs and the mixtures were allowed to react for one hour at room temperature with occasional swirling. Subsequently, the brown dispersions of *eth*-GNF or *cys*-GNF were filtered through a 0.2 µm Whatman polycarbonate membrane to remove any trace of cross-linked flakes. The filtrate was collected, dialyzed against distilled water and then freeze dried to yield the functionalised GNF materials.

4.2 Synthesis of Al-GNFs

A solution of aqueous aluminium chloride (10 mL, 0.1 M) was added to the *cx*-GNFs (10 mg) and the mixture ultrasonicated for 10 min. After this, the aluminium-chelated GNFs (*Al*-GNFs) precipitated out of dispersion and were allowed to settle. The mixture was ultrasonicated again and once again the precipitate formed was allowed to settle. This ultrasonication and settling procedure was repeated one further time. The mixture was then filtered under reduced pressure through a 0.2 μm track-edged polycarbonate membrane. The *Al*-GNFs on the membrane were washed with 3 x 10 mL deionised water to remove any excess aluminium chloride before being left to dry on the membrane under reduced pressure.

4.3 FT-IR spectra of *eth*-GNFs and *cys*-GNFs

FT-IR spectra of *eth*-GNFs and *cys*-GNFs are shown in Fig. S3. The successful chemical functionalisations of the *cx*-GNFs can be seen from the loss of spectral intensity at around 1700 cm^{-1} where the C=O stretching mode of COOH is located (*cf.* Fig. 2(b)).

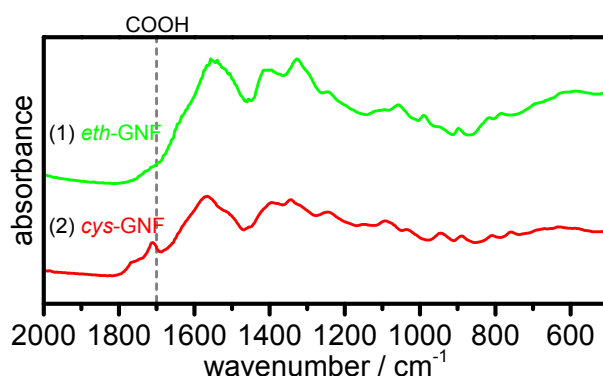


Figure S3. FT-IR spectra of (1) *eth*-GNFs and (2) *cys*-GNFs.

4.4 XPS spectra of *eth*-GNFs, *cys*-GNFs and *Al*-GNFs

The successful chemical functionalisation of the *cx*-GNFs can also be seen from the presence of nitrogen, sulfur and aluminium in the XPS survey spectra shown in Fig. S4.

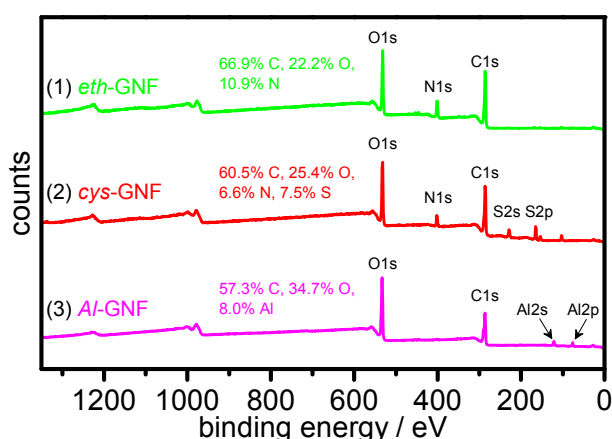


Figure S4. XPS survey spectra of (a) *eth*-GNFs, (b) *cys*-GNFs and (c) *Al*-GNFs.

The high-resolution spectra shown in Fig. S5 give additional information about the oxidation states of carbon, nitrogen and sulfur in the chemically functionalised *cx*-GNF samples. An additional peak in the C1s region of *eth*-GNF is found at around 286.6 eV which is attributed to the methylene (CH_2)

carbon atoms. The N1s region of the *eth*-GNF sample shows two different nitrogen environments corresponding to amine as well as amide nitrogen. As expected, the C1s region for *cys*-GNF also shows a peak for methylene carbon at ~286.5 eV. The N1s and S2p regions show single oxidation states corresponding to amide nitrogen and thiol sulfur, respectively.

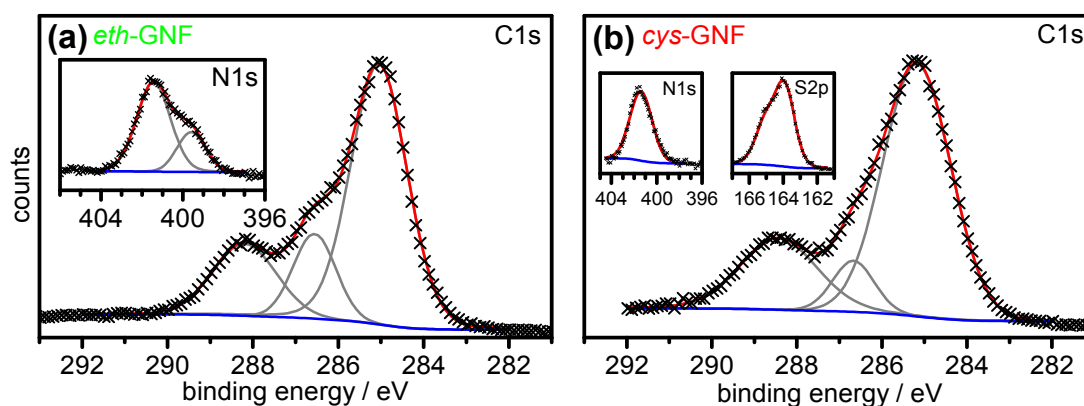


Figure S5. XPS spectra of (a) *eth*-GNF and (b) *cys*-GNF in the C1s region. The N1s and S2p regions are shown as insets. The crosses represent the experimental data, blue line the background, gray lines the fitted peaks and the peak sum is shown in red.

5 TPD-MS measurements

5.1 Detailed analysis of the H₂O and CO₂ desorption from *cx*-GNFs

Figure S6 shows the gas desorption patterns for H₂O and CO₂ from the data shown in Fig. 2(c) recorded upon heating *cx*-GNFs.

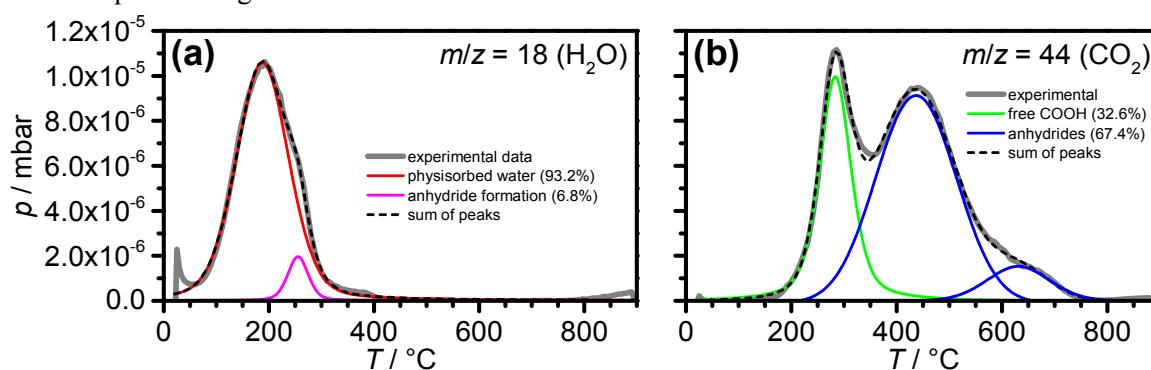


Figure S6. Thermal desorption patterns of *cx*-GNFs at (a) $m/z=18$ (H₂O) and (b) $m/z=44$ (CO₂). The area percentages of the individual components are given in the legend.

Peak fitting with Pseudo-Voigt functions shows that about 93% of the desorbing H₂O originate from physisorbed water. Consistent with the FT-IR spectra shown in Fig. 2(b) the loss of water due to anhydride formation starts at about 200°C. Overall, only about 7% of the desorbing water from the *cx*-GNF sample is due to anhydride formation.

According to the FT-IR analysis in Fig. 2(b) we assign the lower temperature CO₂ desorption peak to the decarboxylation of ‘stranded’ COOH groups which have not formed anhydrides upon heating. The decarboxylation from the anhydride groups takes place at higher temperatures and has a tail on the high-temperature side which we fit with an additional peak. Overall, 67.4% of the desorbing CO₂ originate from the thermal decomposition of anhydride groups and 32.6% are due to CO₂ from ‘stranded’ COOH groups. Considering that two COOH groups are needed to form one anhydride group which then only releases one equivalent of CO₂ upon decomposition, we calculate

that only about 19% of the COOH groups in a *cx*-GNF sample will not form anhydrides upon heating in vacuum.

5.2 Thermal gas desorption patterns of GO

In addition to the thermal desorption data of *cx*-GNFs shown in Fig. 2 we show in Figure S7 the corresponding data for GO. In contrast to our *cx*-GNFs simultaneous desorption of H₂O, CO and CO₂ is observed at around 250°C.

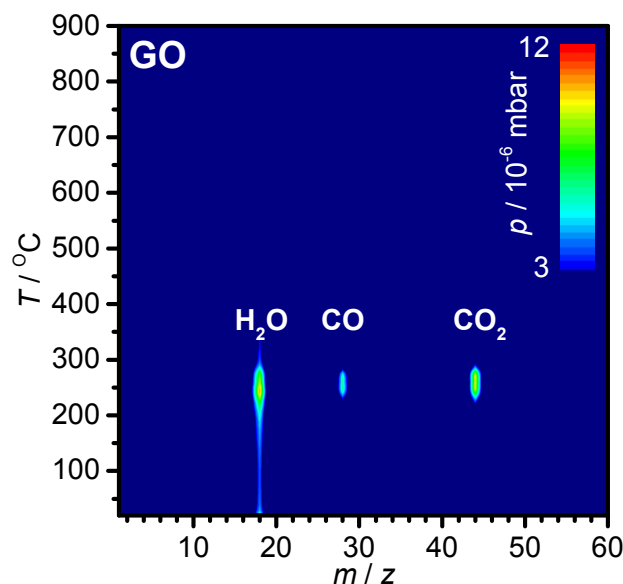


Figure S7. Thermal desorption pattern upon carbonizing 2.5 mg of GO.

6 Transmission electron microscopy (TEM) measurements

In addition to the AFM measurements shown the main article we have also characterised the dimensions of the *cx*-GNFs with TEM. The averages of the shortest and longest lateral diameters calculated from 17 flakes are 16 and 23 nm, respectively.

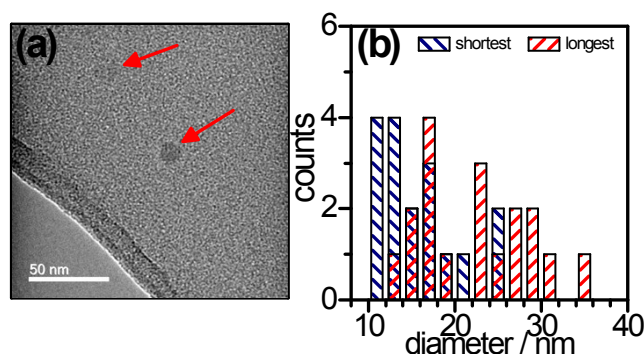


Figure S8. (a) TEM image of two *cx*-GNFs highlighted by arrows. (b) Diameter distribution of the *cx*-GNFs as seen in TEM.

7 Stability of anhydride-containing GNFs (*an*-GNFs) in water and air

The chemical stability of the anhydride groups formed as a result of thermal desorption of H₂O after heating *cx*-GNFs to 285°C was determined by dispersion of *an*-GNFs in water and exposing *an*-GNF

powder to air. The FT-IR spectra in Fig. S8 show that the dispersion in water and exposure to air for 14 days reduced the amount of anhydride groups to the small amount that is present in the as-made material as well (*cf.* Fig. 2(b)).

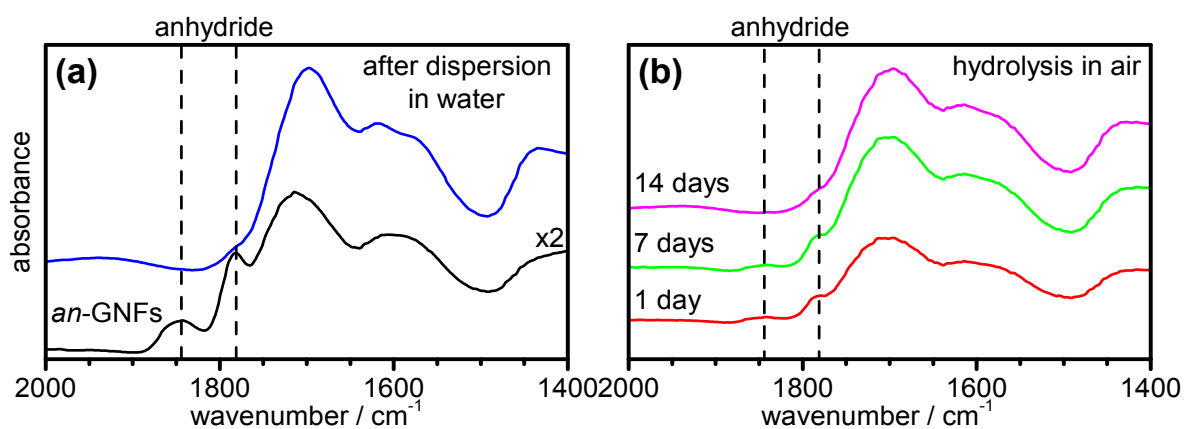


Figure S9. (a) FT-IR spectra of an-GNFs before (black) and after (blue) exposure to liquid water. (b) FT-IR spectra illustrating the hydrolysis of an-GNFs (black) to cx-GNFs upon prolonged exposure to air as indicated by the gradual decrease in the symmetric and asymmetric anhydride stretching modes centered at 1844 cm^{-1} and 1781 cm^{-1} (vertical dashed lines).

8 References

1. J. Chen, B. W. Yao, C. Li and G. Q. Shi, *Carbon*, 2013, **64**, 225-229.
2. W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339-1339.