

Supporting Info for:

Deoxygenation of Graphene Oxide: Reduction or Cleaning?

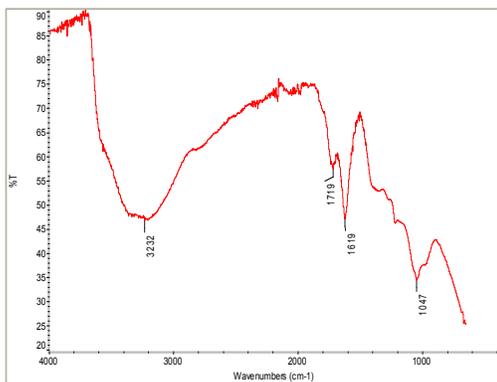
**Helen R Thomas, Stephen P Day, William E Woodruff, Cristina Vallés, Robert J Young,
Ian A Kinloch, Gavin W Morley, John V Hanna, Neil R Wilson and Jonathan P Rourke**

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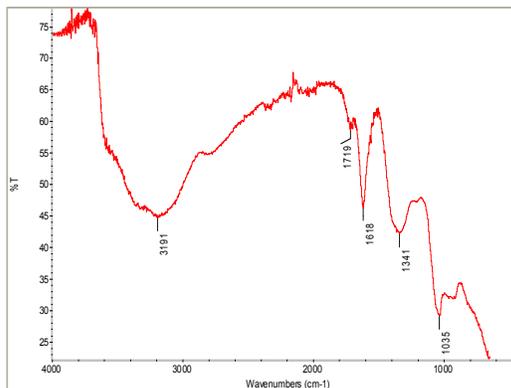
FTIR

FTIR spectra were recorded on a Avatar 320 FTIR spectrometer as solids on a total internal reflectance device.

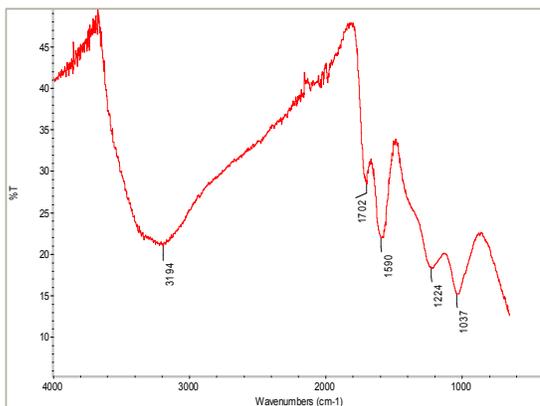
Hummers aGO:



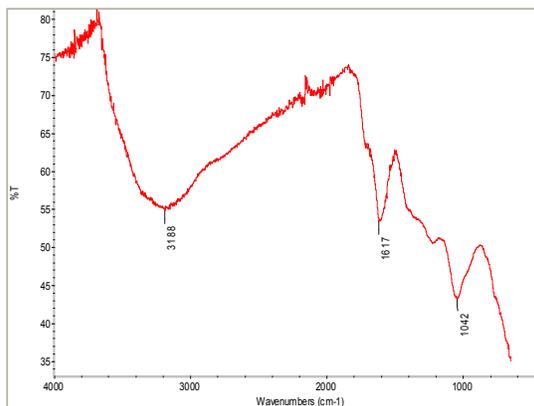
Brodie aGO:



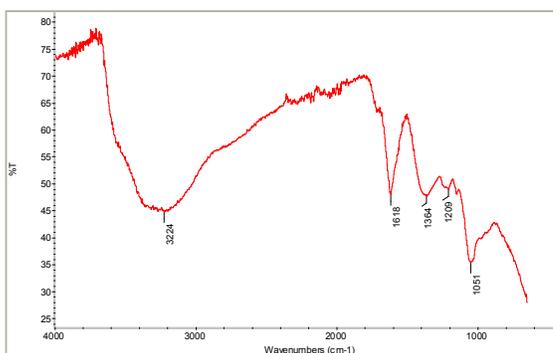
Hummers bwGO (NaOH):



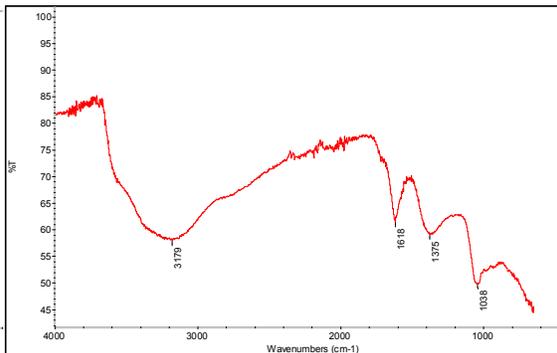
Hummers bwGO (NH₃):



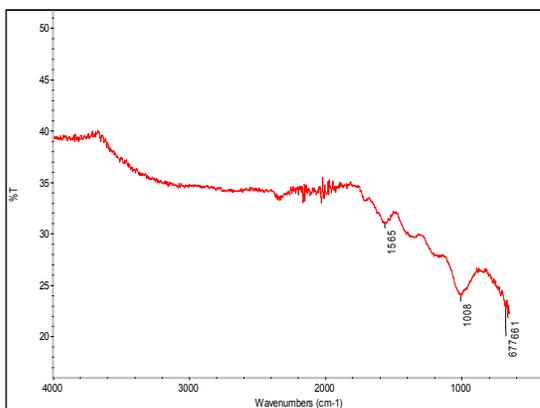
Brodie bwGO (NaOH):



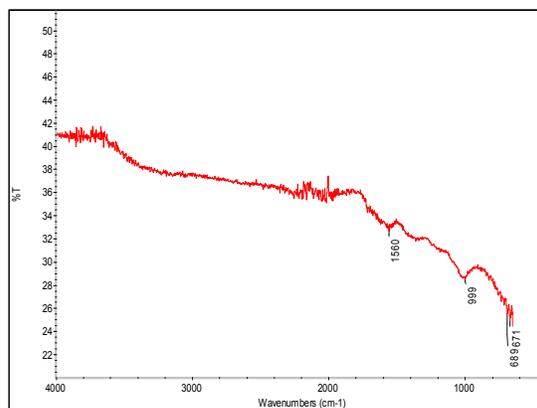
Brodie bwGO (NH₃):



Hummers aGO + N₂H₄ (3hours, RT):



Hummers bwGO + N₂H₄ (1 hour reflux):



“Pristine GO”

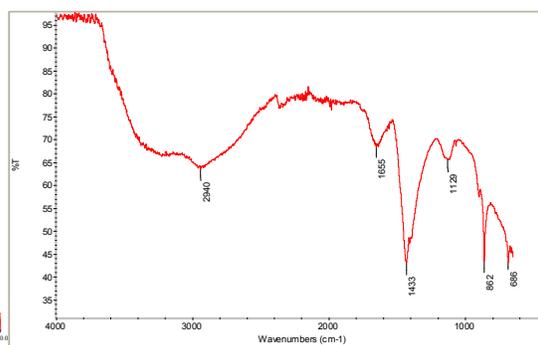
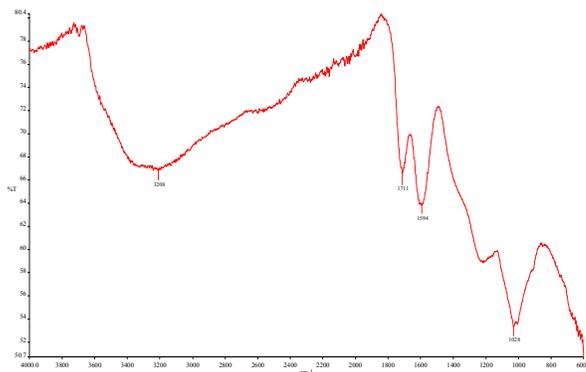
Hydrolysed “Pristine GO”

Dimiev, A.; Kosynkin, D. V.; Alemany, L. B.; Chaguine, P.; Tour, J. M., *J. Am. Chem. Soc.* **2012**, *134*, 2815.



Base-washed hydrolysed “Pristine GO”

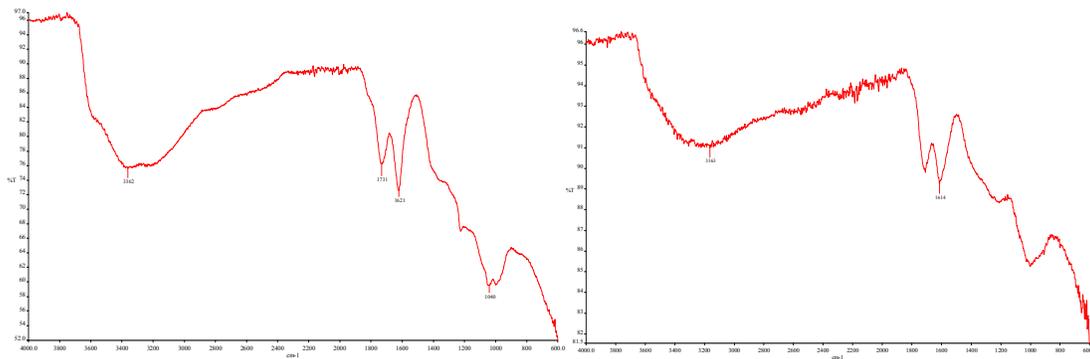
OD (+ NaCl) from bw hydrolysed “Pristine GO”



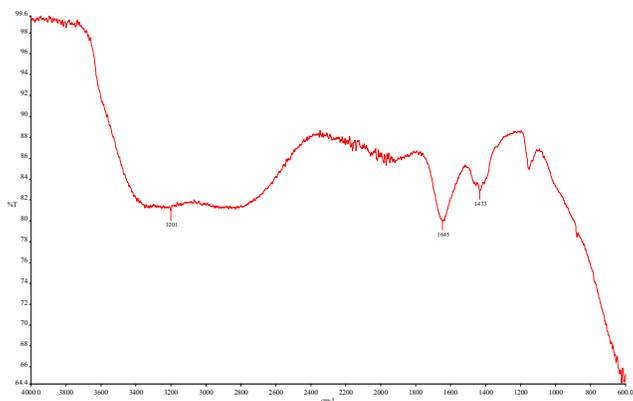
“improved GO”

bw “improved GO”

Marcano, D. C.; Kosynkin, D. V.; Berlin, J. M.; Sinitskii, A.; Sun, Z.; Slesarev, A.; Alemany, L. B.; Lu, W.; Tour, J. M., *Acs Nano* **2010**, *4*, 4806.



OD (+ NaCl) from bw “improved GO”



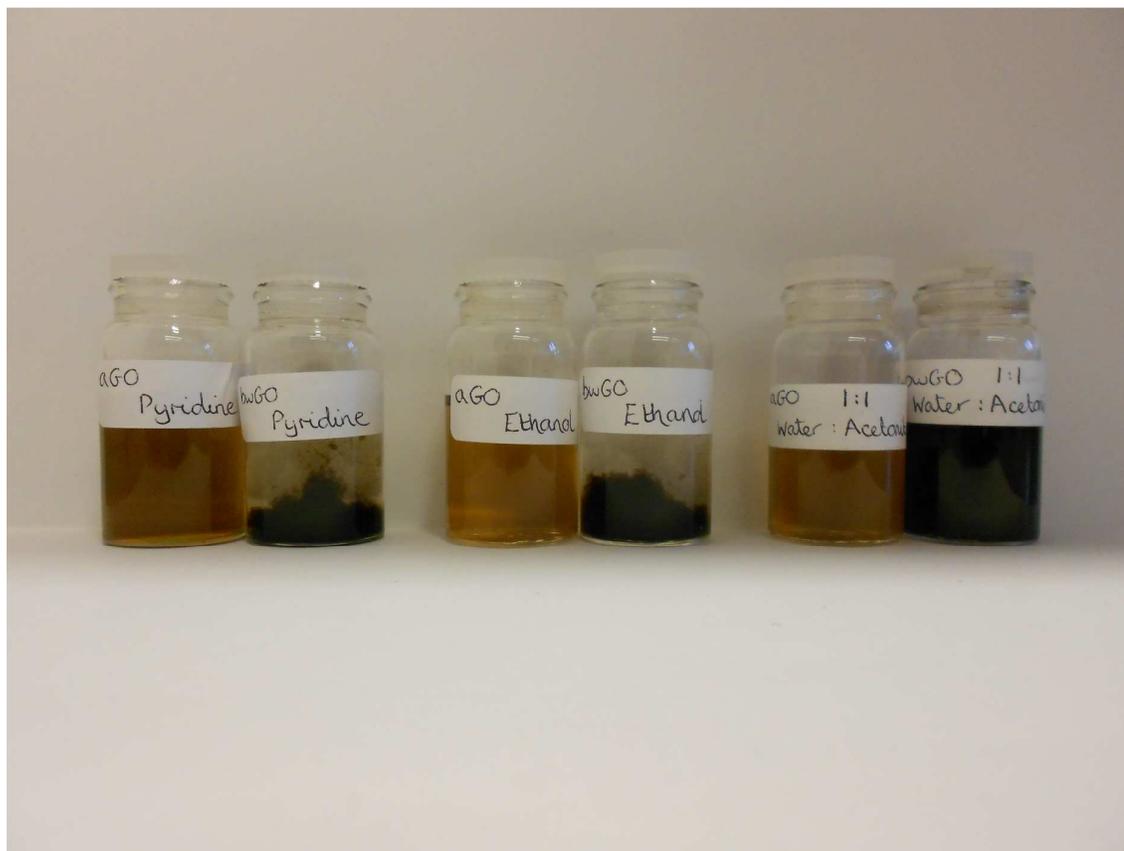
Solubility

aGO and bwGO solutions prepared in a roughly 2:1 water:acetonitrile mixture at 1 mg/ml. 9 ml of solvent added to 1 ml of the 1 mg/ml solutions and the mixtures vigorously shaken. Solubility was assessed immediately and then again after being allowed to settle for 24 hours, but no differences were observed with time, and we consider these dispersions to be stable.

Solvent	Hansen solubility parameters					
	aGO	bwGO	δd	δp	δh	$\delta p + \delta h$
Water	□	□	15.5	16.0	42.3	58.3
DMSO	□	□	18.4	16.4	10.2	26.6
1:1 water:CH ₃ CN	□	□	15.4	17.0	24.2	41.2
DMF	□	□	17.4	13.7	11.3	25.0
IPA	□	□	15.8	6.1	16.4	22.5
Ethanol	□	□	15.8	8.8	19.4	28.2
Pyridine	□	□	19.0	8.8	19.4	28.2
THF	□	□	16.8	5.7	8.0	13.7
Methanol	□	□	15.1	12.3	22.3	34.6
Acetone	□	□	15.5	10.4	7.0	17.4
Acetic acid	□	□	14.5	8.0	13.5	21.5
Acetonitrile	□	□	15.3	18.0	6.1	24.1
Petroleum ether	□*	□*	17.9	0.7	1.8	2.5
Toluene	□*	□*	18.0	1.4	2.0	3.4
Benzene	□*	□*	18.4	0.0	2.0	2.0
Diethyl ether	□*	□*	14.5	2.9	5.1	8.0
Chloroform	□*	□*	17.8	3.1	5.7	8.8

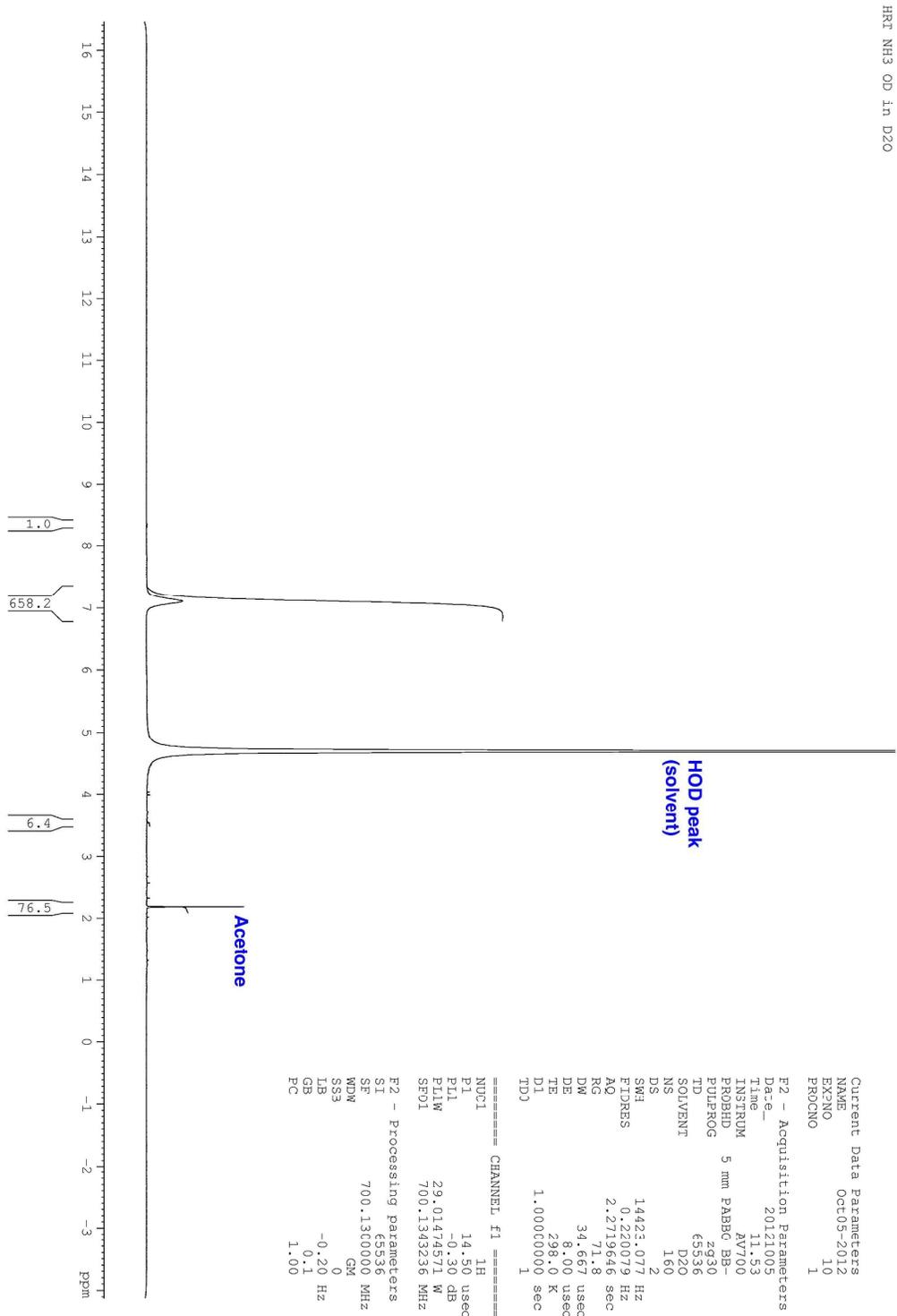
* Immiscible

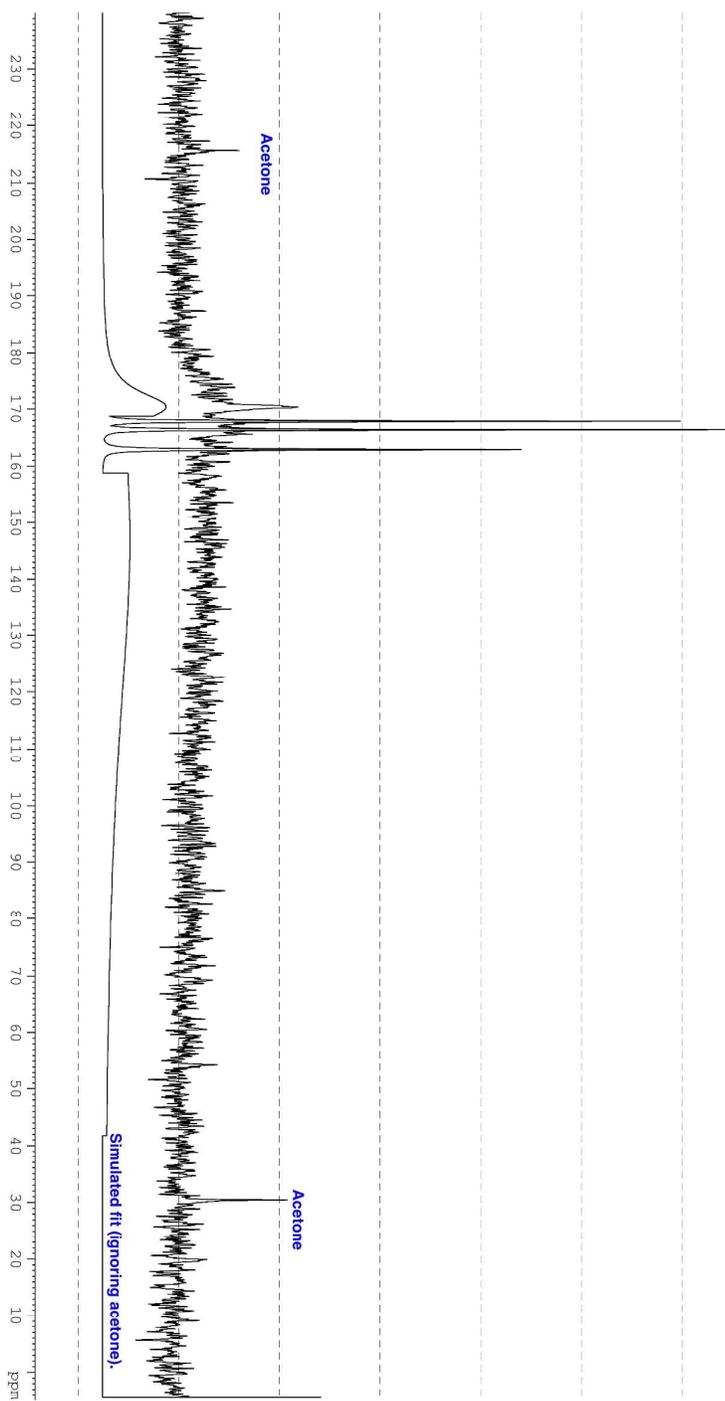
The photograph below shows the differences between the solubilities of aGO (left hand of each pair) and bwGO (right hand of each pair) in three solvents: pyridine, ethanol and 1:1 water/acetonitrile.



Solution NMR

Solution phase NMR spectra of the NH₃ extracted OD from a Hummer's synthesis were run on a Bruker Avance II 700 MHz NMR spectrometer; ¹H (direct observe) and ¹³C (direct observe with gated decoupling); spectra were referenced to external TMS.





Mass Spectrometry

Direct infusion of an aqueous solution of the NaOH extracted OD material from the Hummer's synthesis into a Bruker MaXis high resolution mass spectrometer (electrospray ionisation) gave no meaningful peaks as the instrument response was swamped by the NaCl present. Thus an aqueous solution of the OD material was injected into a reverse phase (C18) LC column and eluted into the mass spectrometer with water/methanol (ramping from 100 % water to 100 % MeOH over 15 minutes). The very first material that eluted from the column was discarded to remove the NaCl. Note that any other hydrophilic low molecular weight ionic species (e.g. oxalic acid, C₂O₄H₂ or trimesic acid C₉O₆H₆) would also be discarded.

The following peaks of significant intensity eluted at later times. Calculated formulas and expected masses are given in parentheses. Note that since all measured peaks have a single positive charge from protonation, the formula of the neutral species has one less hydrogen; also note that we are unable to identify the relative proportions of these materials in the elutant.

209.1168 (C₁₂H₁₇O₃ 209.1172)

213.1479 (C₁₂H₂₁O₃ 213.1485)

227.1275 (C₁₂H₁₉O₄ 227.1278)

305.2774 (C₂₀H₃₃O₂ 305.2475)

309.2050 (C₁₈H₂₉O₄ 309.2060)

319.2283 (C₂₀H₃₁O₃ 319.2268)

337.2376 (C₂₀H₃₃O₄ 337.2373)

353.2680 (C₂₁H₃₇O₄ 353.2686)

359.2428 (C₁₉H₃₅O₆ 359.2428)

393.2122 (C₁₈H₃₃O₉ 393.2119)

481.2654 (C₂₂H₄₁O₁₁ 481.2643)

657.2775 (C₃₁H₄₅O₁₅ 657.2753)

OD collected from an NH₃ wash of Hummer's GO was analysed via the use of a Bruker Ultraflex II MALDI TOF, with the identified matrices, and gave the following ions:

294.070 (C₁₇H₁₂O₄N 294.07665) DHB

335.103 (C₁₉H₁₅O₄N₂ 335.1032) DHB

656.060 (C₃₄H₁₇O₁₃Na 656.0567) CHCA + NaI

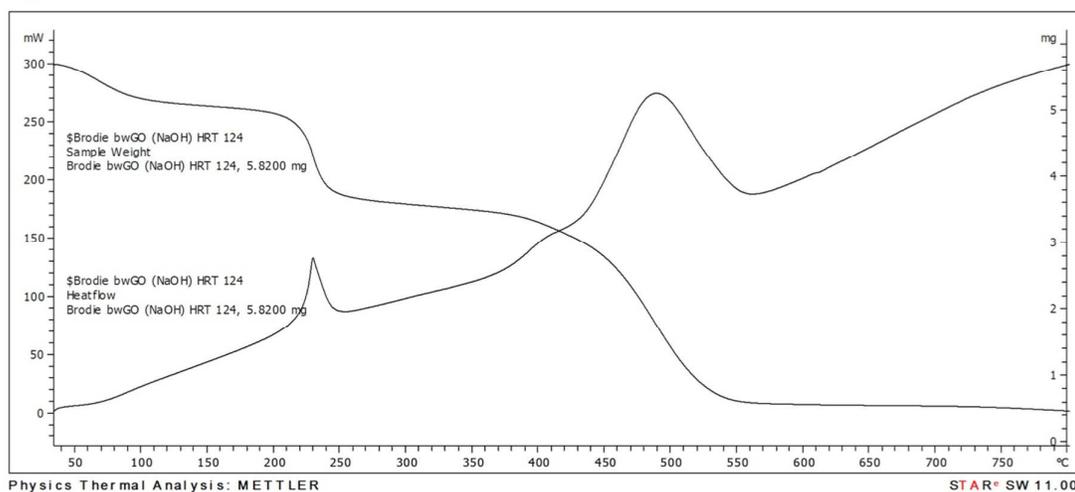
877.089 (C₄₁H₂₃O₂₀N₃ 877.0876) DHB

TGA

All TGA were recorded on a Mettler-Toledo TGA/DSC1 system at a heating rate of 10K/min from 25-800°C under air.

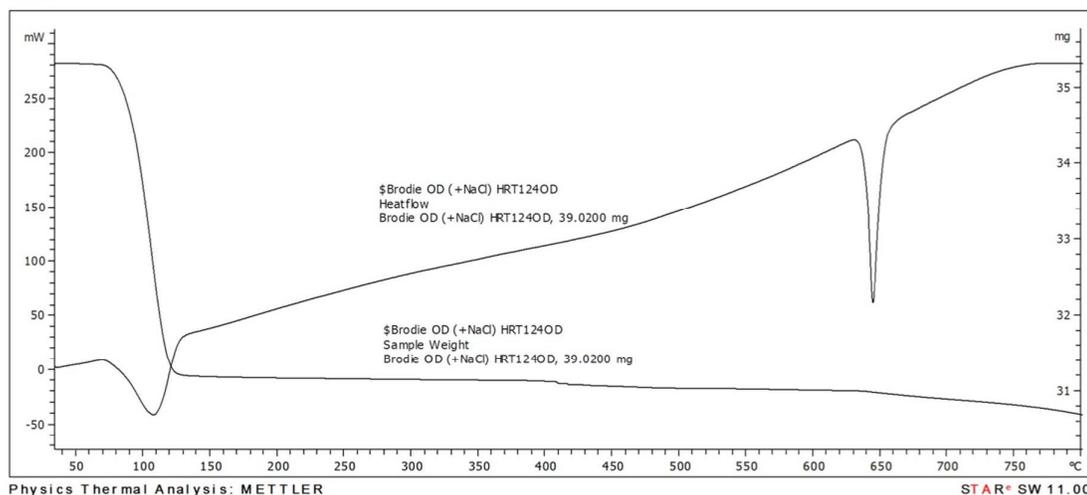
Brodie GO, washed with NaOH

^exo



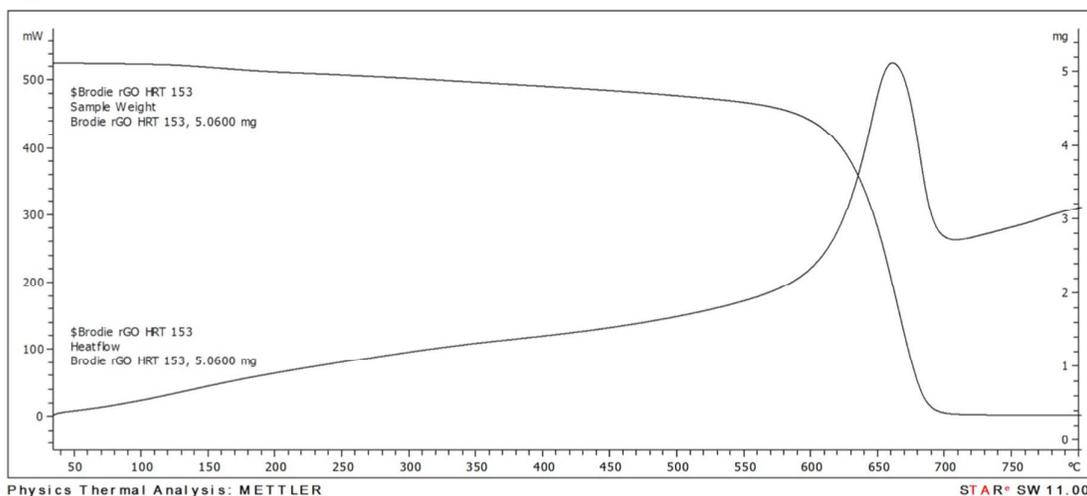
OD collected from Brodie GO when washed with NaOH

^exo



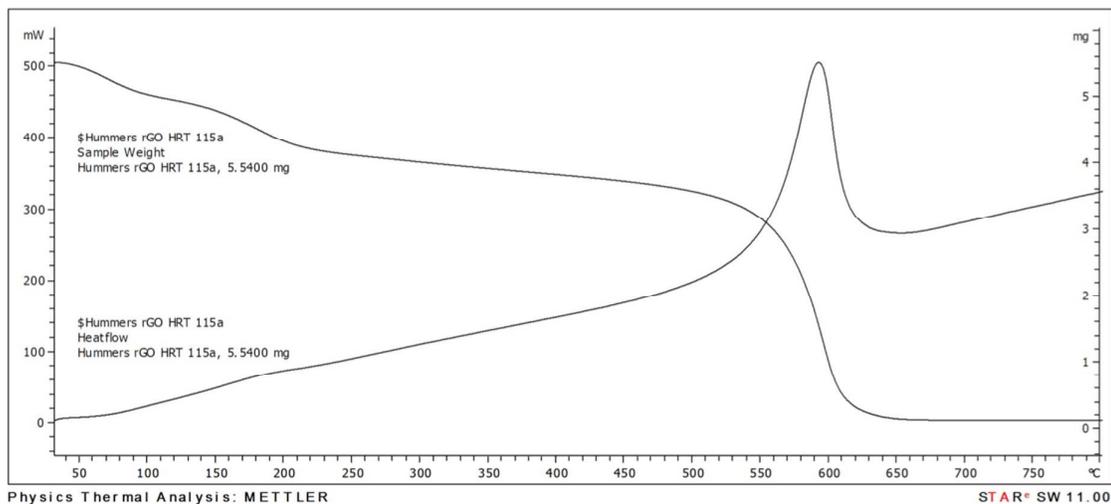
Brodie GO, reduced with hydrazine (1 hour reflux)

^exo



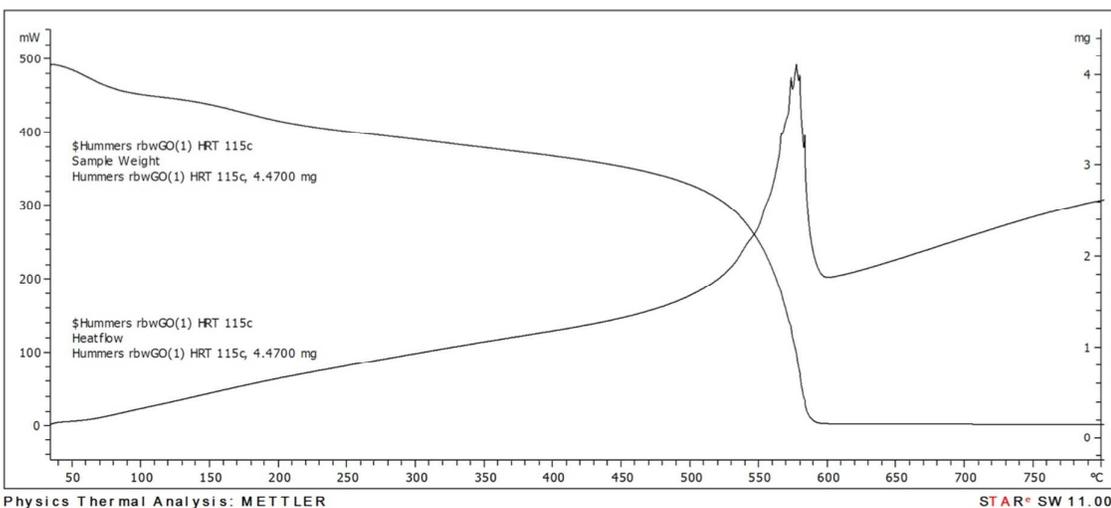
Hummers aGO, reduced with hydrazine (RT, 3 hours)

^exo



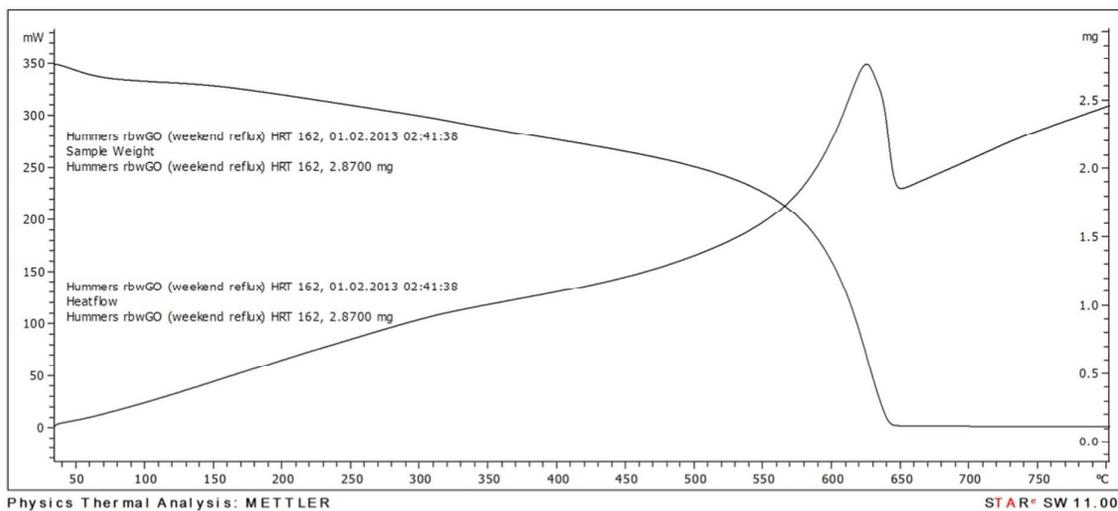
Hummers bwGO, reduced with hydrazine (1hour reflux).

^exo



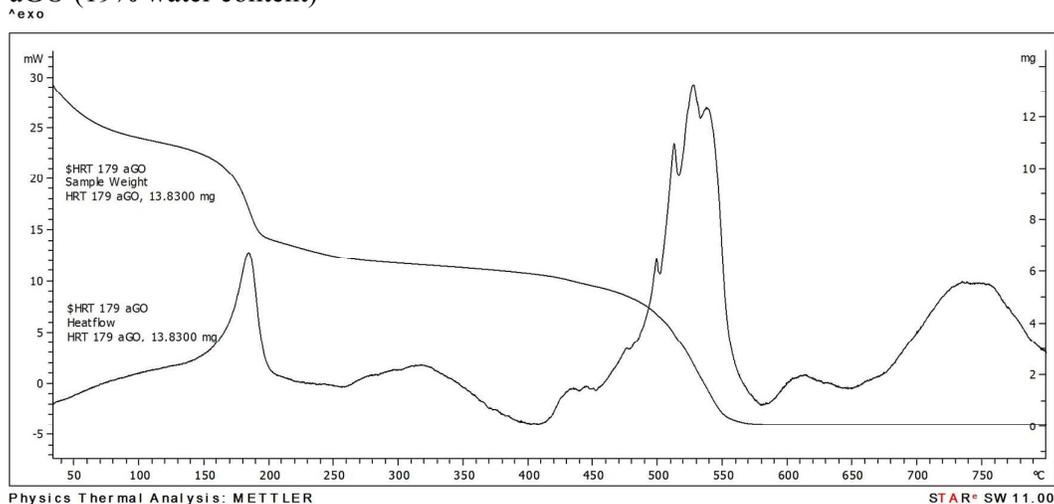
Hummers bwGO, reduced with hydrazine (48 hour reflux).

^exo

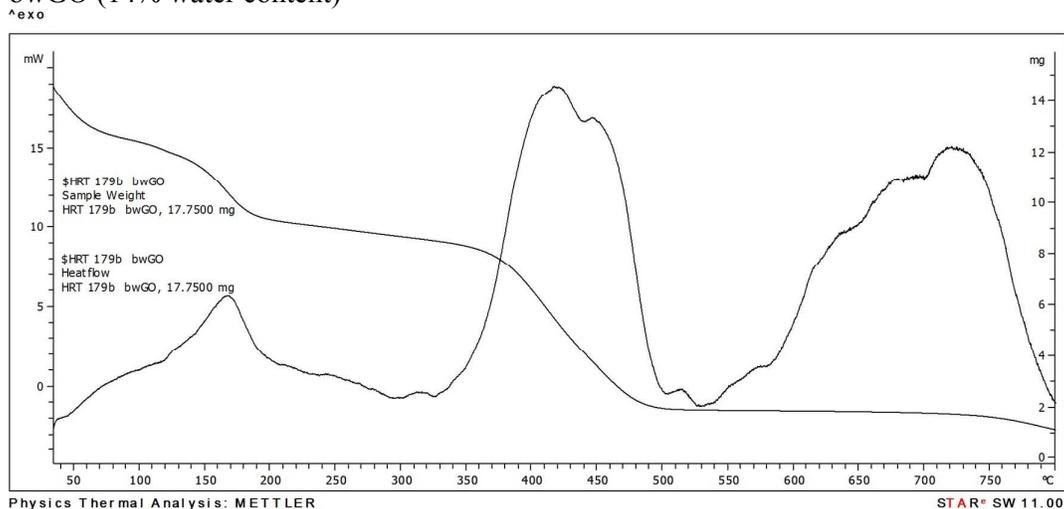


In order to assess the water content, the following three were acquired at a heating rate of 1K min^{-1} . Mass loss below 100°C is assumed to be water.

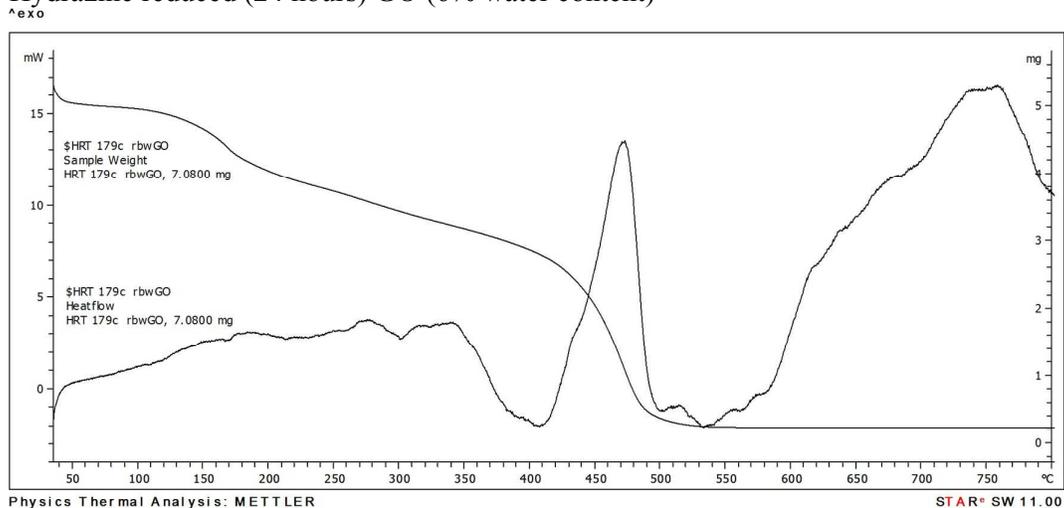
aGO (19% water content)



bwGO (14% water content)



Hydrazine reduced (24 hours) GO (6% water content)

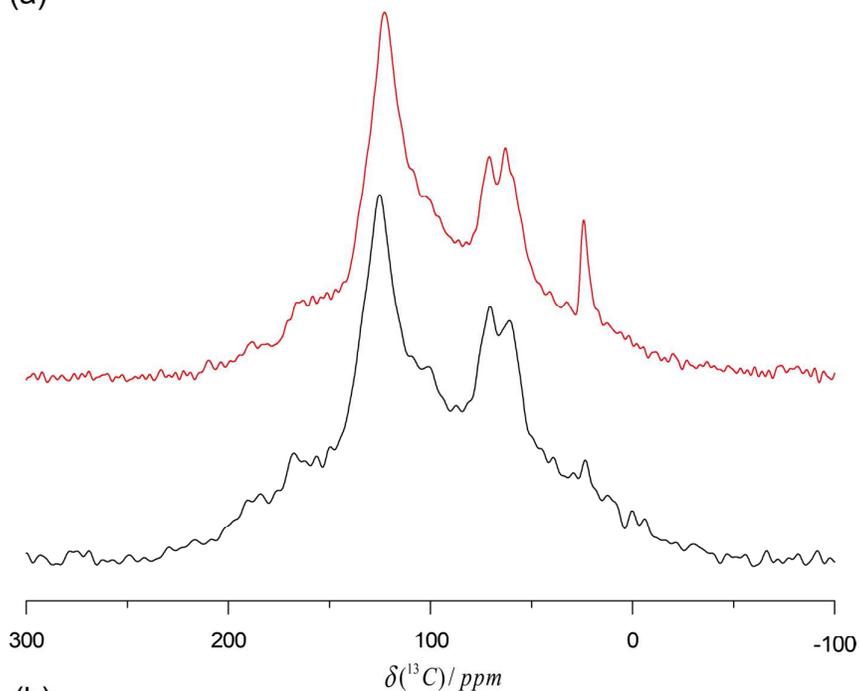


Additional SSNMR spectra

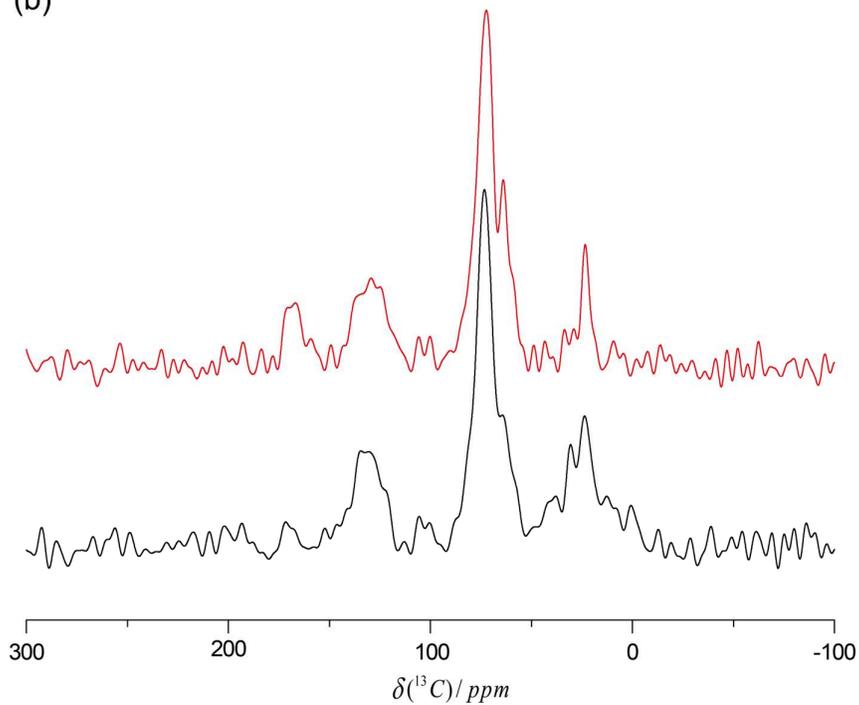
A comparison of base washed Hummers GO, using (red) NH_3 and (black) NaOH .

The spectra in (a) have been acquired via direct single pulse ^{13}C MAS observation, while those in (b) are acquired using a ^1H - ^{13}C CPMAS experiment.

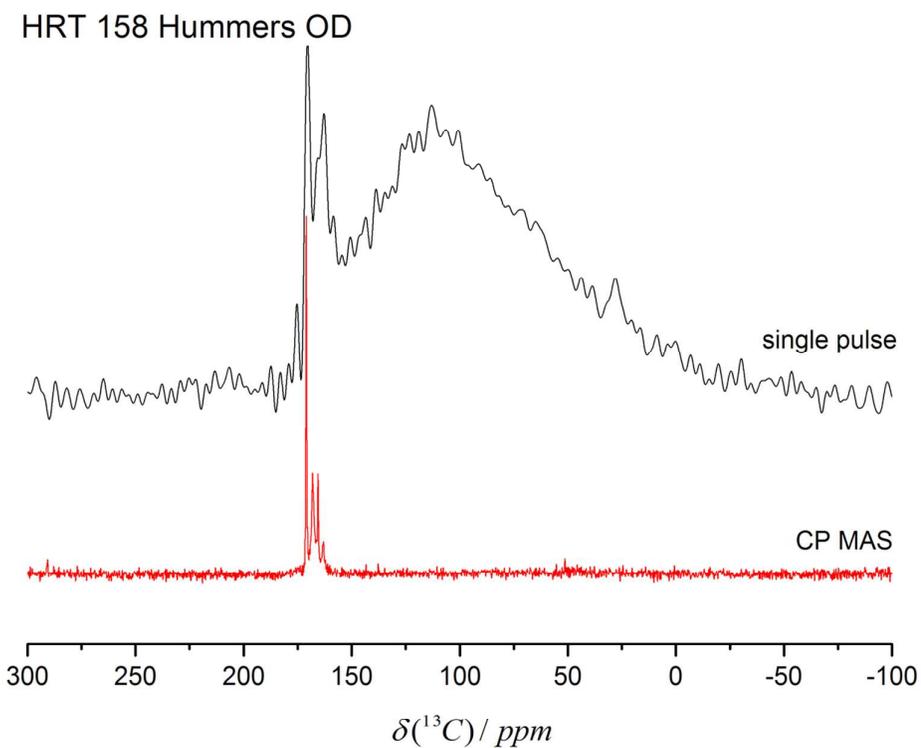
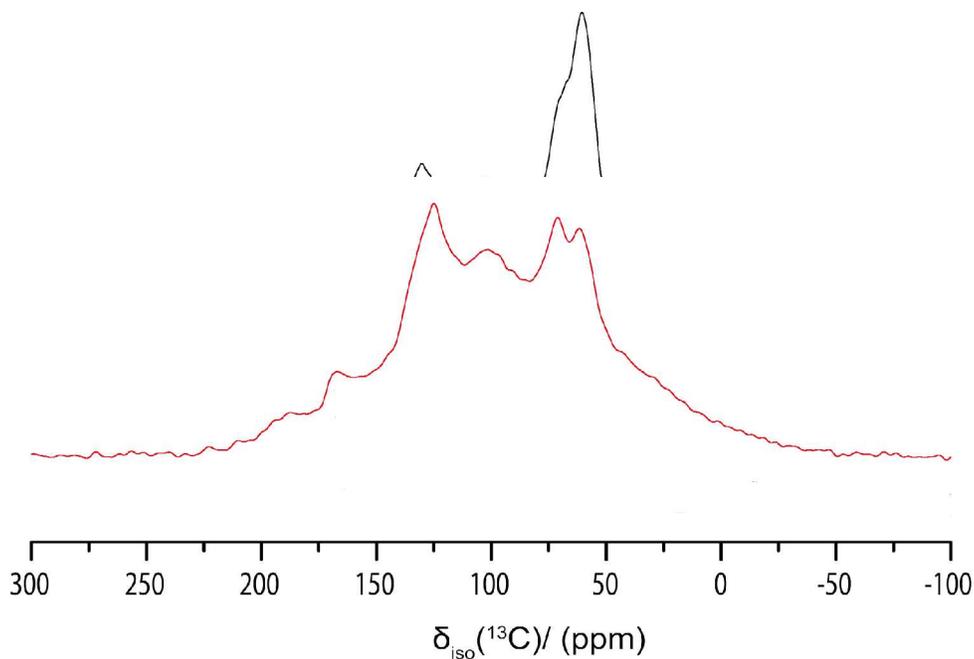
(a)



(b)



Below: a comparison of the aGO produced by the “improved” route (Marcano, D. C.; Kosynkin, D. V.; Berlin, J. M.; Sinitskii, A.; Sun, Z.; Slesarev, A.; Alemany, L. B.; Lu, W.; Tour, J. M., *Acs Nano* **2010**, *4*, 4806.), black line, together with a base-washed sample of the same material (red line).



Detecting Unpaired Electrons in GO

EPR spectra were recorded on a Bruker EMX spectrometer at X-band (around 9.7 GHz). The magnetic field was calibrated with a weak pitch standard sample, and presented with normalization to a microwave frequency of 9.70108 GHz.

The EPR spectra and ssNMR spectra of seven different samples were recorded as follows:

Sample 1: Hummers bwGO

Sample 2: another batch of Hummers bwGO

Sample 3: Hummers aGO

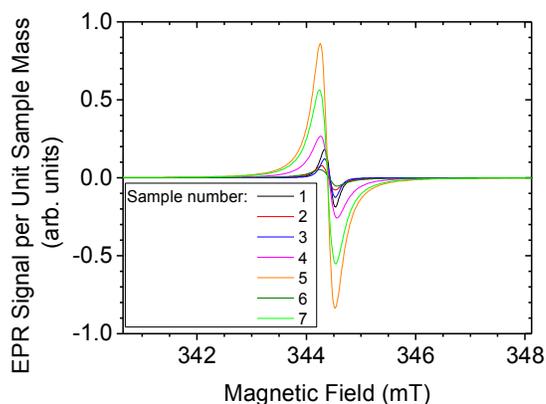
Sample 4: Hummers aGO, treated with hydrazine, RT, 1 hour

Sample 5: Hummers bwGO, treated with hydrazine, RT, 3 hours

Sample 6: Hummers bwGO, treated with hydrazine, reflux, 1 hour

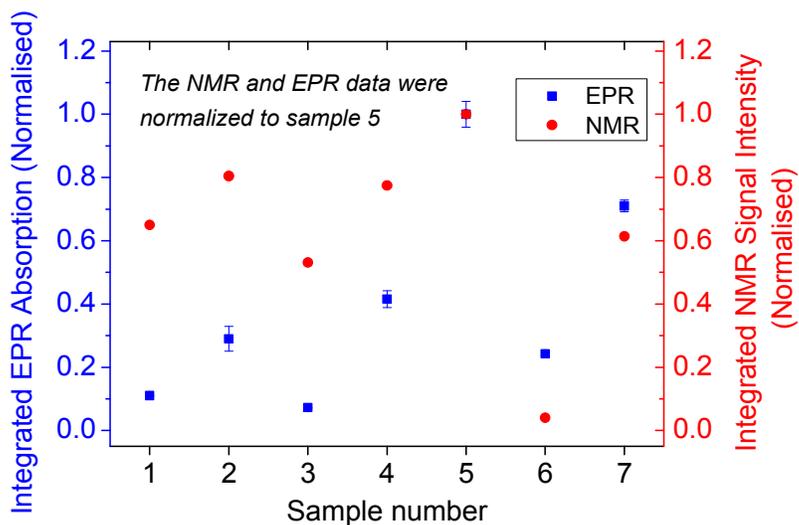
Sample 7: Hummers bwGO, treated with hydrazine, RT, 11 hours

All of the samples showed very strong EPR signals, shown below, indicating the presence of unpaired electron spins. We expect to see both conduction electrons and dangling-bond defects. We did not take any steps to de-oxygenate the samples, which has been found to be important for nanostructured graphite,¹⁻² but not for reduced graphene oxide.³



The figure below shows a correlation between the relative number of electron spins as measured in EPR and the magnitude of the broad peak centred on 110 ppm in the ssNMR (see Fig 1, main paper). Absolute spin counting in the EPR was not attempted; the EPR will see all of the unpaired electron spins, while NMR will only see those that are coupled to ^{13}C . All EPR spectra could be fitted ($R^2 > 0.99$) with a Gaussian resonance plus a Lorentzian resonance, but depending on the sample, the ratio of Gaussian/Lorentzian varied from 0.2% to 72%, and the linewidths varied from 0.29 to 10 mT. A linewidth of 0.66 mT was reported previously for reduced graphene oxide made with the Hummers method, but the g -factor of 2.0030 ± 0.0002 differs significantly from our measurement of 2.0125 ± 0.0001 . Some of our EPR spectra show six-line hyperfine signals from manganese,³ (presumably present as an

impurity from the synthesis) but the intensity is too small to be significant, or even visible in the figure above.



Sample 1: Hummers bwGO, Sample 2, Hummers bwGO, 3 aGO, etc

- (1) Kausteklis, J.; Cevc, P.; Arčon, D.; Nasi, L.; Pontiroli, D.; Mazzani, M.; Riccò, M., *Phys. Rev. B* **2011**, *84*, 125406.
- (2) Osipov, V. Y.; Shames, A. I.; Enoki, T.; Takai, K.; Endo, M.; Hayashi, T.; Kaburagi, Y.; Vul, A. Y., *Diamond Relat. Mater.* **2009**, *18*, 220.
- (3) Panich, A. M.; Shames, A. I.; Aleksenskii, A. E.; Dideikin, A., *Solid State Commun.* **2012**, *152*, 466.