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Supporting Information

Using Nuclear Magnetic Resonance Proton Relaxation to Probe the Surface Chemistry of Carbon 2D Materials

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Materials and Methods

Materials and sample preparation

A total of seven graphitic powders were measured, as provided by an industrial manufacturer. These included an unfunctionalized graphitic starting material (G), and the same material functionalised by employing a plasma treatment process with various degrees of oxygen- and nitrogen-containing chemical groups (Table S1).

Briefly, according to the manufacturer, the functionalisation process involved placing the unfunctionalised graphene in a HDPlas® plasma reactor with a gas feed containing the elements needed for the functionalisation. The feed gas was allowed into a low-pressure chamber where it was energised and ionised to create a plasma. Samples were mixed during the plasma treatment to ensure homogeneity of functionalisation.

To vary the degree of functionalisation (low, medium, and high), the intensity of the plasma processing was progressively increased. The functional groups (nitrogen and oxygen) are expected to be covalently bound to the graphitic materials.

Table S1. List of graphitic samples.

Sample name	Sample Code	Functionalisation Expected from treatment
G	12397	Unfunctionalised
O-low	13039	Low degree of oxygen-containing functional groups
O-med	13040	Medium degree of oxygen-containing functional groups
O-high	13092	High degree of oxygen-containing functional groups
N-low	13042	Low degree of nitrogen-containing functional groups
N-med	13043	Medium degree of nitrogen-containing functional groups
N-high	13044	High degree of nitrogen-containing functional groups

Graphitic powders were shaped into disc pellets (7 mm diameter) by mechanical compression using a hydraulic press (Specac, Orpington, UK) and a force of 1-2 tons, for use with XPS and Raman spectroscopy analyses.

Graphitic dispersions were prepared gravimetrically for use in NMR proton relaxation experiments. Solvents employed included dimethyl sulfoxide (DMSO, Reagent Grade 99.5 %, Fisher Scientific, UK), 1-methyl-2-pyrrolidone (NMP, ACS reagent, ACROS Organics™), toluene (anhydrous, 99.8 %, Sigma Aldrich), isopropyl alcohol (IPA,_>=99.5%, A.C.S. REAGENT, Sigma Aldrich), and ethanolamine (ethanolamine, 99% ACROS Organics™). Each dispersion was prepared independently to minimise the measurement uncertainty of the dilution factor. For each sample/solvent combination, a minimum of 5 dispersions were prepared with concentrations ranging from ~1 mg/mL to ~20 mg/mL (depending on the sample/solvent combination). Dispersions were sonicated for 5 minutes in an ultrasonic bath at a frequency of 37 kHz and 80 W ultrasonic power (CamSonix C275T, Camlab, Cambridge, UK). This short sonication time was selected in an effort to break aggregates/agglomerates, while maintaining the structural integrity of the sample.[1]

Diluted dispersions (roughly 0.01 mg/mL) in DMSO (10 µL) were drop-cast on silicon wafers with a native oxide layer at the boiling point of the solvent (roughly 189 °C) for SEM analyses.

Methods

SEM – Images were collected using a Zeiss (Oberkochen, Germany) Supra Microscope by measuring secondary electrons (In lens detector, 30 µm aperture, 5 kV accelerating voltage, 2048 pixel x 1536 pixels; mean pixel size: 9.4 nm ± 5 nm). Images were then analysed using SPIP software (Version 6.7.5, Image Metrology A/S, Denmark). The lateral size of at least 200 particles was determined by measuring the length (longest edge-to-edge distance) and width (a perpendicular bisector of the length) of the particles and calculating the mean value of the two.[1] Particles were only measured when they could be clearly distinguished from the background, and their edges were clearly defined. The histogram of each set of lateral size data was fitted to a lognormal distribution using OriginLab (OriginPro, Version 2019b, OriginLab Corporation, Northampton, MA, USA) software. Each sample was described in terms of the median and standard deviation of the fitted lognormal function. The median lateral size and the lognormal standard deviation are computed from the fitted lognormal distribution fit parameters using formulas from the NIST Engineering Statistics Handbook, section 1.3.6.6.9, *Common Statistics.*[*]

Nitrogen physisorption – A minimum of 100 mg of powder sample was loaded inside an analysis tube (tubes were weighed empty and then filled with sample and weighed again after degassing) for each sample. Samples were initially degassed overnight (minimum of 12 hours) in an external degas unit FlowPrep060 (Micromeritics, UK) by flowing nitrogen gas (nitrogen (oxygen free), BOC, Surrey, UK) over the samples at 130 °C (or 300 °C). A low nitrogen flow rate (< 50 cm^3/min) was employed to avoid aerosolisation of the powder samples. After the degas step, samples were kept under flowing nitrogen gas until at room temperature. Samples were weighed immediately after degassing and placed onto the sorption analyser (ASAP 2460, Micromeritics, UK) for gas sorption analysis. The samples were then evacuated in the sorption analyser down to at least 0.7 Pa with a low evacuation rate (~0.1-0.2 kPa/s) at ambient temperature. Helium (helium (A grade), BOC, Surrey, UK) was employed to measure the free-space volume at the start of the analysis. Afterwards, all samples were evacuated again in the analyser under the same conditions for 30 minutes. The analysis was then performed by employing nitrogen as a probing gas at liquid nitrogen temperature. The saturation pressure of nitrogen was measured at each isothermal point. A minimum of 6 points were collected in the relative pressure range of 0.01-0.30 P/P_0, P_0 being the saturation pressure of the adsorptive. The BET plot was then employed to calculate the surface area from nitrogen sorption isotherms.[2]

$$\frac{1}{V\left[\left(\frac{P_0}{P}-1\right)\right]} VS \frac{P}{P_0}$$

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[*] https://www.itl.nist.gov/div898/handbook/eda/section3/eda3669.htm

Where V = volume of gas adsorbed at a relative pressure; P = equilibrium pressure of the gas (derived from the isotherm); P_0 = saturation pressure (derived from the isotherm).

A molecular cross-sectional area of 0.1620 nm^2 was employed for nitrogen in the BET calculation.[3]
The range of relative pressures over which BET theory was applied was chosen to obtain: i) a positive C value, ii) a positive intercept, iii) a correlation coefficient greater than 0.9999 and iv) increasing $V\left(1-\frac{P}{P_0}\right)$ with increasing $\frac{P}{P_0}$.[4] Each measurement was repeated at least 3 times and an average BET SSA was reported. The measurement uncertainty is expressed as the standard deviation (σ) between individual measurements and reported as 3σ.

XPS - The surface chemistry of graphitic pellet samples was characterised with X-ray photoelectron spectroscopy (XPS), using a Kratos Axis Ultra DLD (Kratos Analytical, Manchester, UK) equipped with a monochromatic Al Kα X-ray source (operated at 15 kV anode potential and 5 mA emission current). During acquisition, the analyser was operated in 'hybrid' lens mode with the 'slot' entrance slit, which defines an analysis spot on the sample of 300 µm × 700 µm. Survey spectra between 1350 eV and -10 eV were collected with a pass energy of 160 eV, a step size of 1 eV, 200 ms dwell time, and 2 sweeps. Narrow scans were acquired for the C 1s, N 1s, and O 1s core levels with a pass energy of 20 eV, a step size of 100 meV, 500 ms dwell time, and 3 sweeps. A set of survey and narrow scans was acquired for 3 areas on each sample; no significant differences were observed between the analysis areas. Charge neutralization with a low-energy electron source was not required as none of the samples showed evidence of charging. Transmission function corrected spectra were analysed using the CasaXPS software (Version 2.3.19) in conjunction with the average matrix relative sensitivity factors (AMRSF) published by the National Physical Laboratory (NPL) [5–7] in order to determine elemental composition. For all spectra, the Tougaard background type was employed, although a linear background was used when the decay of the inelastic background was dominant. Elemental composition was calculated from each survey spectrum collected from 3 different areas per sample and reported as an average. The relative uncertainty of quoted atomic percentages due to peak area measurement is ±10 %. These uncertainties assume a completely flat sample surface with a homogeneous composition throughout the XPS information depth (<10 nm).

Raman spectroscopy – Confocal Raman spectroscopy was carried out using an inVia Qontor spectrometer (Renishaw, UK) on pelletised graphitic powders. A 532 nm laser was employed with a 100× objective lens (0.85 numerical aperture), with a power at the sample of 0.13 mW (1 % laser power) with a 2400 l/mm grating. Spectra were acquired with 2 s exposure for each measurement location. For each sample, spectra were recorded from 2 locations on the pellet, at each location a map with a 10 µm × 10 µm area (1 µm step size) was measured, for a total of 242 spectra per sample. Prior to peak fitting the spectra were processed using WiRE software (Version 5.1) by removing signal artefacts due to cosmic rays, subtracting a polynomial background and then normalizing the spectra to the peak with the highest intensity. Each spectrum was fitted individually to Lorentzian functions using the WiRE software and the relative maximum intensities and FWHM were calculated for each spectrum. The standard deviation was also calculated from 3 repeat measurements.

NMR spin-spin relaxation – Graphitic dispersions were prepared as described in the “Materials” section and added into NMR tubes (100 MHz, 5 mm diameter) using long Pasteur pipettes, immediately after vigorous mixing (~ 1 min vortex). Care was taken to fill the NMR tubes to the same height for each measurement (roughly 55 mm between the meniscus of the solution and the lower end of the tube). NMR tubes were then sealed with PTFE tube caps to prevent solvent evaporation. Spin-spin (T2) relaxation experiments were performed in an Acorn Area benchtop NMR from Xigo Nanotools (Orefield, PA, USA) operating at approximately 13 MHz. Prior to the start of the analysis, the resonance frequency was tuned with a standard test dispersion provided by Xigo Nanotools. The laboratory temperature was monitored in close proximity to the equipment and was observed to be relatively stable (21.0 ± 0.1 °C). The relaxation time (T2) was measured with a Carr-Purcell-Meiboom-Gill (CPMG) method.[8]

T2 spin-spin relaxation experiments were performed as opposed to T1 spin-lattice experiments, due to the reduced measurement times of T2 experiments, which minimise any settling of graphitic dispersions. A similar trend may be expected from T1 spin-lattice experiments, although the extent of the relaxation enhancement with surface chemistry may differ in the two methods.[9] The T2 CPMG sequence employs a 90° pulse (6.78 µs) followed by a series of 180° pulses (13.56 µs). The time between the initial 90° and 180° pulse is termed τ, and 180° pulses are repeated every 2* τ. A τ of 0.5 ms has been employed for all measurements. An echo occurs following each 180° pulse until the signal decays. The average peak value of each echo is then plotted as a function of time. A scan is an application of this sequence of pulses. The number of echo cycles for each scan is calculated automatically from the software algorithm so that the total duration of the scan is 5 x T2. The first scan is a “dummy” and is not used in the calculation of T2, the subsequent scans are averaged to calculate Mxy(t), which is fitted to a single exponential with an offset to calculate T2. A total of 4 scans were averaged in each experiment, as no significant effect on the resulting T2 values was observed as you increased the number of scans from 4, to a total of 15 scans. The recycle delay between each scan was set to 5 x T2. The measurement parameters were selected based on a chosen T2 value, which was first estimated by the user and then corrected based on the subsequent measurement result. Measurements were repeated until the initially chosen T2 values were within 20 % of the measured values.

At this point, the measurement was repeated three times and results averaged. Samples were mixed in between each repeat to minimise any effect due to settling. The measurement uncertainty is calculated as the standard deviation of the three measurement repeats and reported as 3 σ.

Recycle delay – T2 experiments were repeated in samples with different concentrations, solvents and surface chemistries, using recycle delays of 5 x T1 and 5 x T2, to compare any potential effect of the recycle delay on the measurement of T2. T1 relaxation times were calculated for each sample employing the inversion recovery method.[10] T2 results are reported in Table S2 and did not show any significant change with the recycle delay employed. Therefore, a recycle delay of 5xT2 was chosen to allow for reduced measurement times, which will avoid particles settling and is better suited for rapid quality control purposes.

Table S2. Comparison of T2 spin-spin relaxation times measured with a CPMG sequence, varying recycle delays.

Sample type	**T2 relaxation times (ms) ± standard deviation**	
	Measured using a recycle delay of:	
	5 x T1	**5 x T2**
G in DMSO (high concentration)	272.1 ± 3.0	272.1 ± 0.3
G in DMSO (low concentration)	866.7 ± 2.4	865.7 ± 4.4
O-high in DMSO	189.4 ± 0.6	188.5 ± 1.2
G in NMP	170.4 ± 1.5	173.6 ± 1.7

Supporting Figures

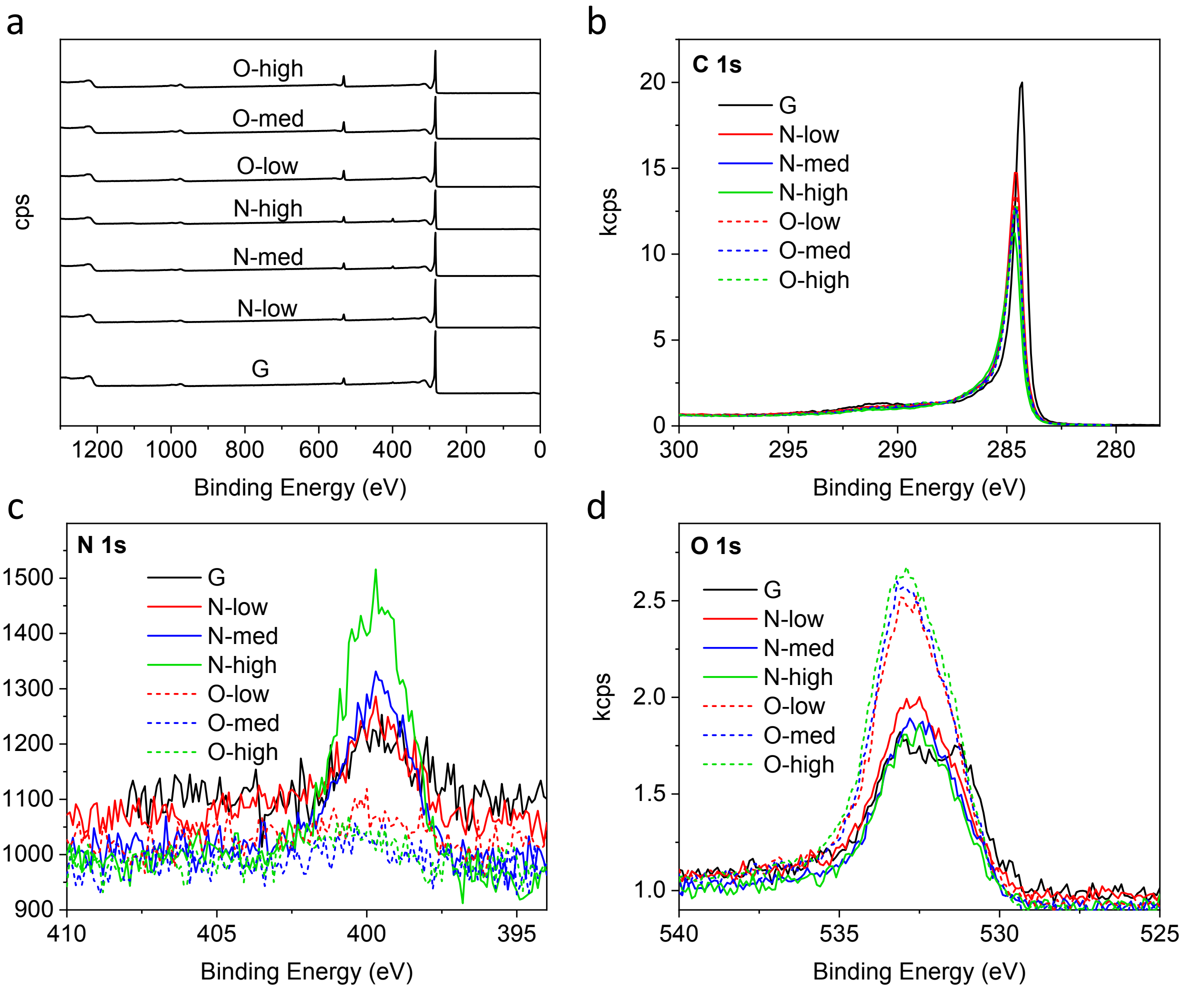

Figure S1. XPS spectra (a) Survey and (b-d) high resolution spectra for C 1s, N 1s, O 1s for all samples in counts per second (cps).

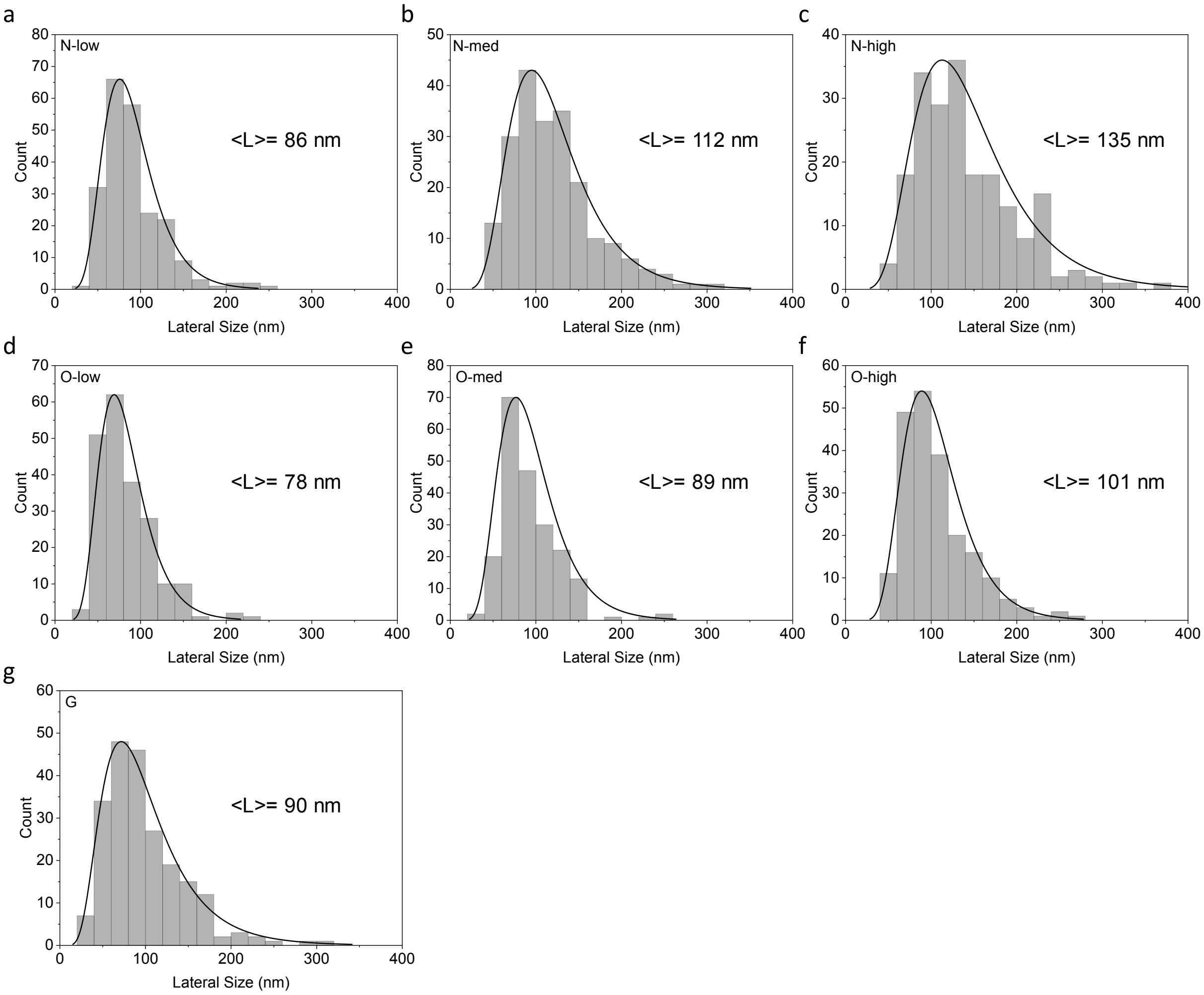

Figure S2. Number-based lateral size distributions and their lognormal fits resulting from the analysis of over 200 particles from SEM images. <L> indicates the lognormal median lateral size.

Table S3. Average lateral size resulting from the analysis of over 200 particles from SEM images.

Sample name	Lognormal median from over 200 particles (nm)	Lognormal standard deviation from over 200 particles (nm)
G	90	35
N-low	86	23
N-med	112	35
N-high	135	45
O-low	78	21
O-med	89	26
O-high	101	27

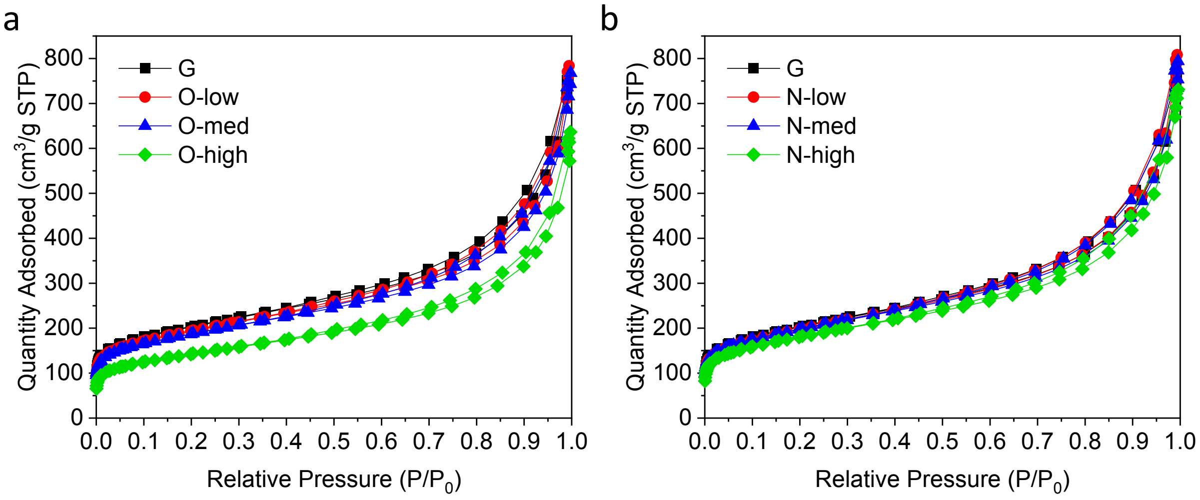

Figure S3. Nitrogen physisorption isotherms measured at 77 K for all samples. Materials were pre-degassed at 130 °C under nitrogen gas prior to the start of the analysis.

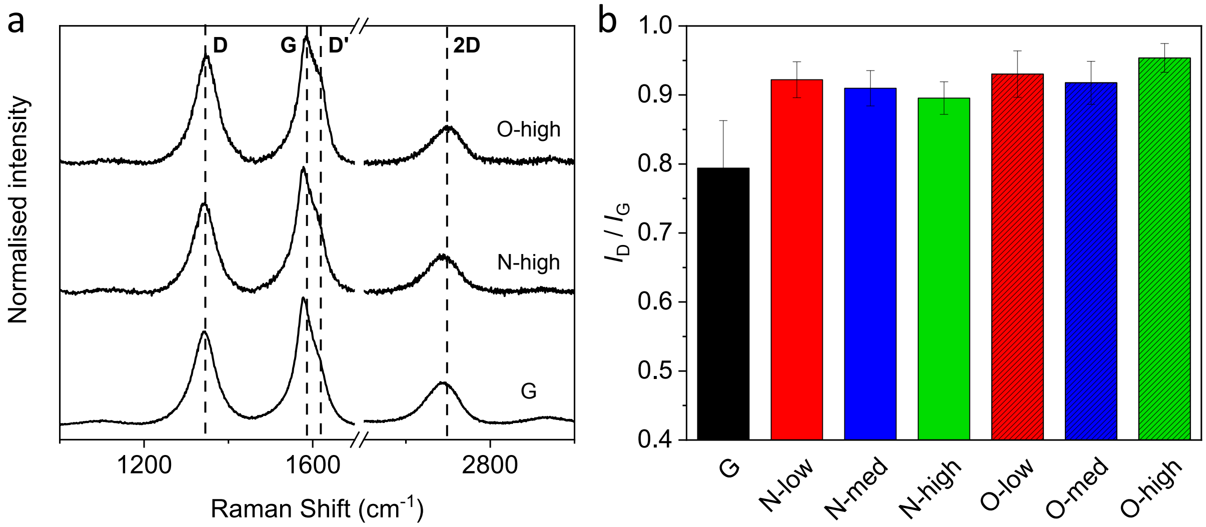

Figure S4. Raman spectroscopy a) Average spectra for 3 representative samples and b) ratio of modal intensities of D-peak vs G-peak for all samples.

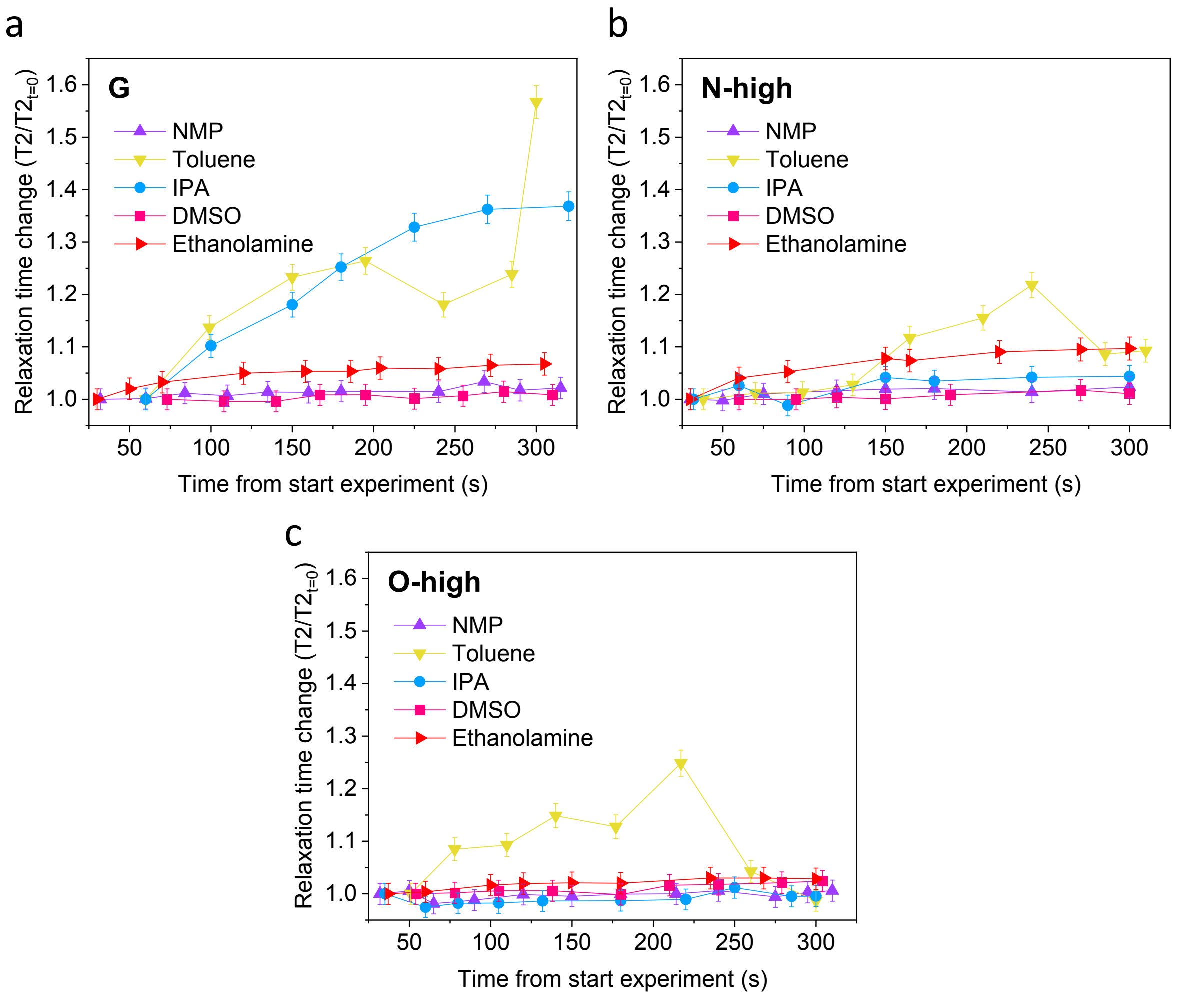

Figure S5. Stability of dispersions in different solvents – Relaxation time T2 relative to T2 at t=0 of graphitic dispersions in various solvents as a function of the time since the dispersion was added into NMR tubes. For toluene, after ~150 s the magnetisation decay curve is not a single exponential anymore, so T2 measurements become inaccurate.

Table S4. Slopes in relaxation rate *vs* weight ratio of graphitic materials in DMSO

Sample	**Slope (ms^{-1})**
G	0.161 ± 0.003
N-low	0.181 ± 0.004
N-med	0.173 ± 0.004
N-high	0.172 ± 0.007
O-low	0.209 ± 0.004
O-med	0.213 ± 0.004
O-high	0.250 ± 0.003

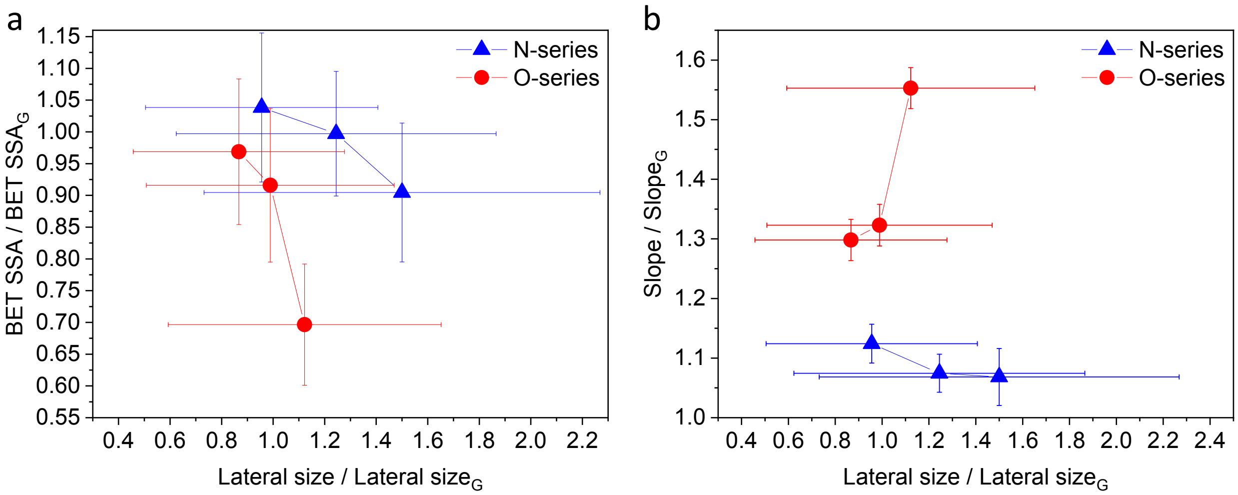

Figure S6. Relative comparisons – a) BET SSA vs lateral size measured via SEM normalised by the values for sample G; b) Slope of R_{av}/weight ratio (from Figure 2) vs lateral size, normalised to sample G.

Table S5. Literature values for Dispersive (D), Polar (P) and Hydrogen bonding (H) Hansen solubility parameters for the solvents used in this study and for graphene.[11,12]

Material/solvent	**δ_D (MPa$^{1/2}$)**	**δ_P (MPa$^{1/2}$)**	**δ_H (MPa$^{1/2}$)**
NMP	18.0	12.3	7.2
DMSO	18.4	16.4	10.2
IPA	15.8	6.1	16.4
Toluene	18.0	1.4	2
Ethanolamine	17.0	15.5	21.0
Graphene	18.0	9.3	7.7

Hansen sphere solubility radius (R) equation: $\sqrt{4 \cdot (\delta_D - \delta_{D,G})^2 + (\delta_P - \delta_{P,G})^2 + (\delta_H - \delta_{H,G})^2}$

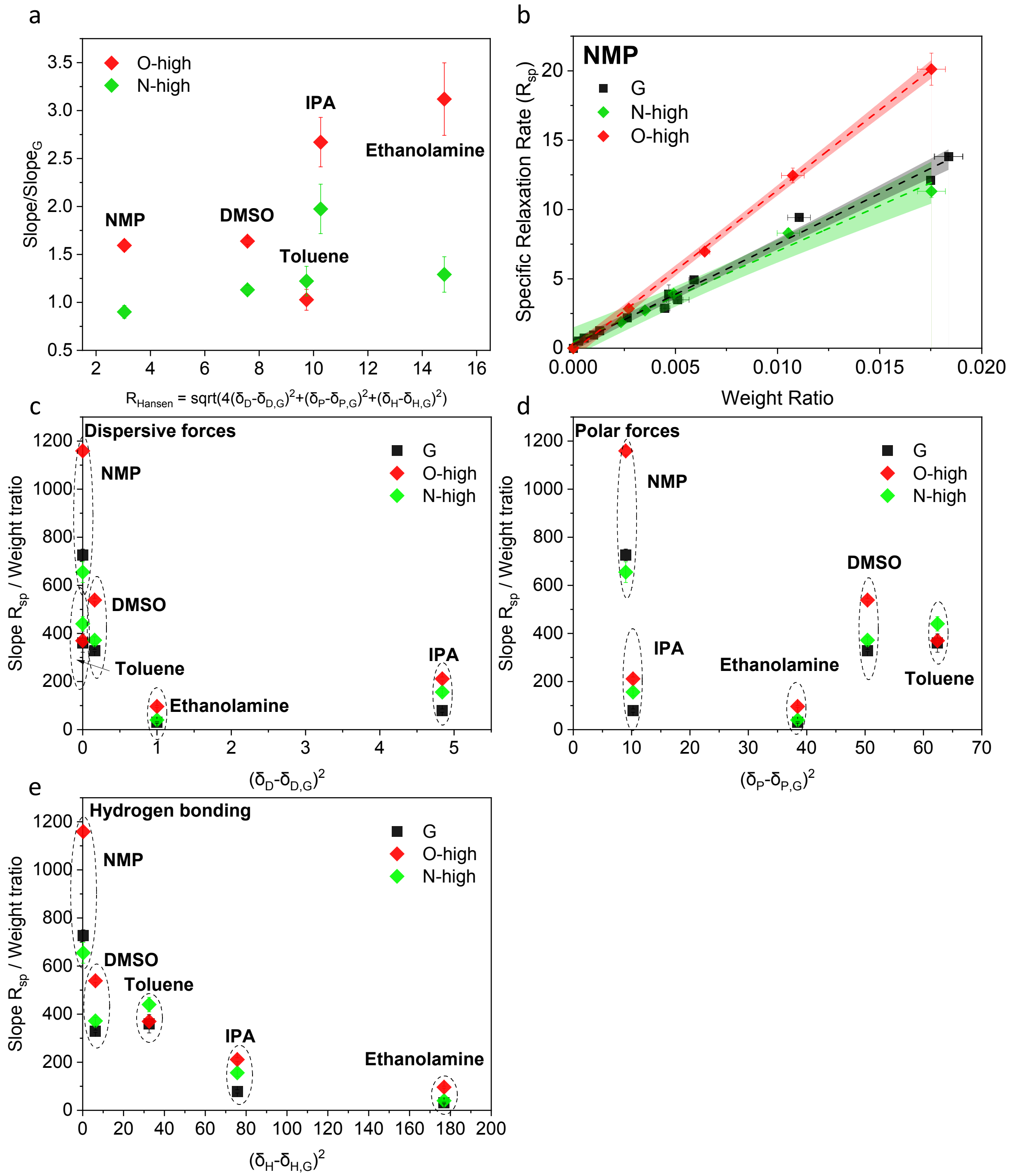

Figure S7. Solvent effect – a) Gradient of R_{sp} divided by weight ratio normalised to sample G, for O-high and N-high in different solvents, versus the radius (R) of the Hansen solubility sphere for graphene; b) specific relaxation rate *vs* weight ratio for three samples in NMP; c-e) Individual contributions from Hansen solubility parameters for three samples in different solvents.

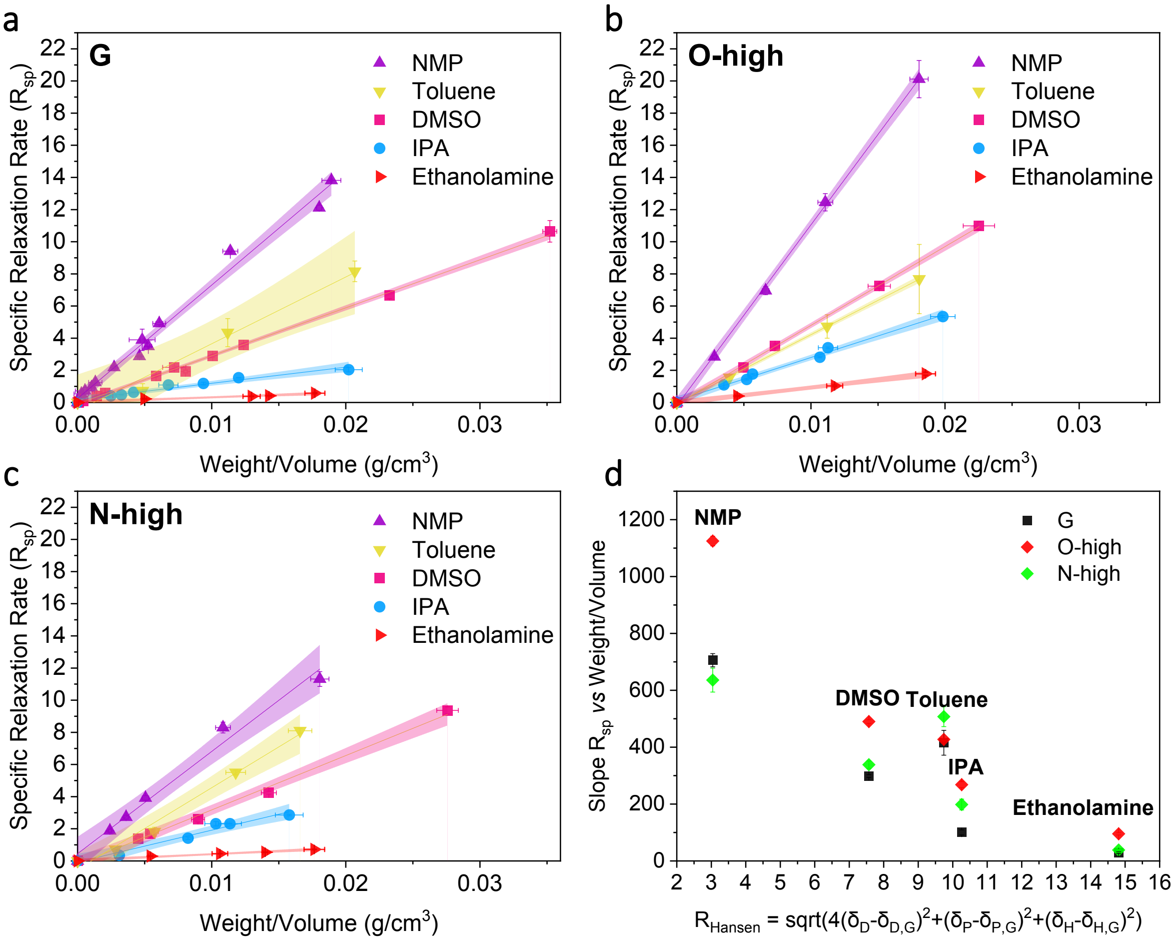

Figure S8. **NMR proton relaxation in different solvents** –Specific relaxation rates of graphitic dispersions as a function of concentration with linear fits and 95 % confidence bands for: a) unfunctionalised material (G), b) O-high and c) N-high; d) calculated gradient of specific relaxation rate vs weight to volume ratio for three samples in different solvents, plotted against the Hansen solubility sphere radius for graphene.

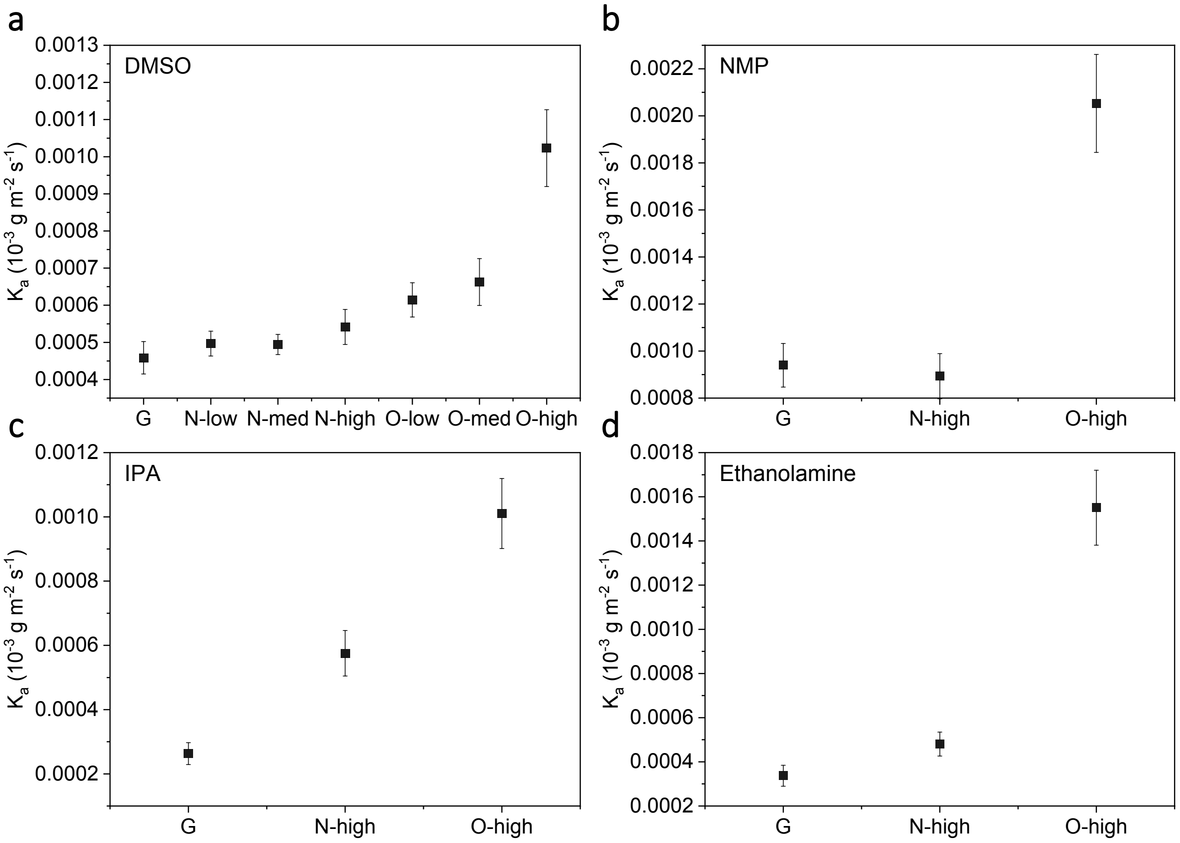

Figure S9. Specific surface relaxivity – K_a calculated for all samples assuming NMR SSA equal to BET SSA, assuming the density of all graphitic samples to be 2.2 g/mL and the density of the solvents to be: 1.1 g/mL for DMSO, 1.0 g/mL for NMP, 0.8 g/mL for IPA and 1.0 g/mL for ethanolamine.[†] The units are reported as $10^{-3}\ g \cdot m^{-2} \cdot s^{-1}$ which are equivalent to $g \cdot m^{-2} \cdot ms^{-1}$.

[†] https://organicchemistrydata.org/solvents/; Ethanolamine density from Sigma Aldrich

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