- Supplementary Data -

Solvent-free functionalisation of graphene oxide with amide and amine groups at room temperature

Stefania Sandoval[a], Amparo Fuertes[a] and Gerard Tobias.[a,*]

Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Campus de la UAB, 08193 Bellaterra (Barcelona), Spain.

1.   Experimental

1.1.   Synthesis of graphene oxide (GO): Graphene oxide was synthesized by a modified Hummer's method.[1] Concentrated H_2SO_4 (115 mL) and $NaNO_3$ (2.5 g) were added slowly to graphite powder (5g) (< 20 µm, Sigma-Aldrich), and the mixture was cooled down to 0 °C. After 30 min, $KMnO_4$ (15 g) was added slowly in order to keep the temperature below 20 °C. The reaction was warmed to 35 °C and stirred for 30 min. Afterwards, the mixture was cooled to room temperature and 230 mL of water were added slowly maintaining the reaction temperature at 98 °C for 2 h. Then, additional water (1 L) and 30 % H_2O_2 solution (5 mL) were added slowly. The content was air cooled and purified washing with distilled water, followed by centrifugation until the pH of the solution was neutral.

1.2.   Synthesis of nitrogen functionalised GO (N-GO): 100 mg of GO were spread into a sintered Al_2O_3 boat and placed into a silica tube in the presence of pure ammonia gas (Carburos Metálicos 99.99%) with a flow rate of 300 mL.min^{-1}. In order to study the effect of the time of treatment in the degree of functionalisation of the samples, the samples were kept in the system during 5, 15, 30 and 60 minutes, respectively. Afterwards, the powder was kept under vacuum during 3 h to eliminate possible physisorbed molecules. Two additional experiments were performed keeping the

starting GO within systems saturated with NH_3 atmosphere. For this purpose, 100 mg of sample were placed inside a 25 mL round bottom schlenk, the atmosphere of the system was purged by at least three argon-vacuum cycles and pure ammonia gas was subsequently flown at 500 mL/min during 1.5 min. Afterwards the system was hermetically closed keeping the sample inside during 60 min. The procedure was repeated including magnetic stirring to the system. Both samples were evacuated under vacuum during 3 h.

1.3.   Synthesis of N-doped RGO:

An additional sample, doped at 500 ℃ during 1 h in NH_3 flowing at 300 mL.min^{-1} was prepared for comparison.[2]

1.4.   Characterisation:

Elemental analyses data were recorded on a Thermo Scientific™ FLASH 2000 Series CHNS Analyzer using a Metler Toledo MX5 microbalance. Analyses were performed at least on two replicas (ca. 1 mg).

The morphology of the sheets was studied using microscopic imaging. Samples, previously dispersed in absolute ethanol (sonication), were placed dropwise onto a lacey carbon support grid and characterised recording SEM, TEM images and SAED patterns. TEM images and SAED patterns were obtained using a JEOL 1210 microscope, operating at 120 kV. SEM images were obtained using a Quanta FEI 200 ESEM FEG microscope, operating at 10.0 kV.

Thermogravimetric analyses were performed on a Netzsch instrument, model STA 449 F1 Jupiter®, under flowing air at a heating rate of 10 ℃.min^{-1}. TGA-MS data were acquired in a TGA/SDTA851e/LF/1600 coupled to a THERMOSTAR GSD301T detector.

Diffraction patterns were recorded in a Siemens D5000 diffractometer (Kα Cu λ= 1.5418 Å). 2θ values were acquired at 0.02 ° intervals between 5 ° and 70 °. Samples were measured as solid powders using a glass slide as a support. The acquired data was not further processed and directly plotted.

XPS were recorded in a Kratos AXIS ultra DLD spectrometer using monochromatic Al Kα. All samples were introduced in the preparation chamber as received and on the same substrate (Cu) to maintain the analysis conditions invariable. High resolution spectra of C1s, O1s and N1s regions were also registered.

The XPS data was acquired at the Laboratorio de Microscopías Avanzadas (LMA) - Instituto de Nanociencia de Aragón (INA), and EA in the Centres Científics i Tecnològics - Universitat de Barcelona, both in Spain.

1.4.1. Quantification of the -NH$_2$ loading:

Calibration curve of hexylamine. A calibration curve resulting from the reaction of hexylamine and ninhydrin was prepared. 2 mL of a 3.03 x 10^{-3} M hexylamine stock solution in absolute ethanol (Sigma-Aldrich) were mixed with 2 mL of ninhydrin (6 % in absolute ethanol, Sigma-Aldrich) and the mixture was refluxed (99 °C) under continuous stirring during 90 min. After cooling down, different aliquots of the obtained product (Ruhemanns blue) were diluted with 60 % ethanol solution to obtain solutions with concentrations ranged between 7.5 x 10^{-6} M and 3.63 x10^{-4} M. The absortion spectra of the solutions were recorded using a Varian Cary 5 spectrophotometer in the 800 nm and 400 nm range. The maximum absorbance point (λ_{max}) was plotted vs the concentration of the corresponding solution. A mixture of the stock solution (2 mL) and 2 mL of absolute ethanol was refluxed at the same conditions of the initial reaction and made up to 10 mL with 60 % ethanol solution. This was employed as reference.

Determination of the -NH$_2$ loading in the N-containing RGO samples. 0.5-5 mg of the corresponding sample were introduced in a round-bottom flask and refluxed with 2 mL of a 6 % ninhydrin solution during 90 min. After cooling down, the suspension was centrifuged at 4200 rpm for 15 min and the supernatant was made up to 25 mL. The absorbance of the solution was measured in the 800 nm and 400 nm range. Tentagel^{TM} HL-NH$_2$, a commercial primary amine resin (Sigma-Aldrich) with a 4 x 10^{-4} mol· g^{-1} -NH$_2$ loading was employed as control material. Behenamide (CH$_3$(CH$_2$)$_{20}$CONH$_2$, analytical standard, Sigma-Aldrich) was also tested to discard false-positive results due to the presence of amides on the sample.

## 2. Elemental Analysis of Graphene Oxide and ammonia treated samples

Table S1. Composition of C and N present in GO and ammonia treated samples (at room temperature) determined by elemental analysis (wt. %).

Time	Flow of NH$_3$ (mL.min^{-1})	C (wt. %)	STD	N (wt. %)	STD
5 min	100	54.9	0.11	3.3	0.02
5 min	300	51.5	0.74	3.6	0.22
15 min	300	52.3	0.12	3.8	0.03
30 min	300	54.2	0.06	4.2	0.07
60 min	300	54.2	0.38	4.4	0.06
60 min	100	54.0	0.36	5.2	0.03
60 min	1000	53.9	045	4.0	0.07
60 min	*	55.2	0.41	4.0	0.03
60 min	**	54.5	0.28	3.7	0.03

 * Sample stirred in a round bottom flask in the presence of a NH$_3$ saturated atmosphere.
** Sample placed inside a silica tube in the presence of a NH$_3$ saturated atmosphere (no stirring).

## 3. Identification of the inserted groups and thermal behaviour
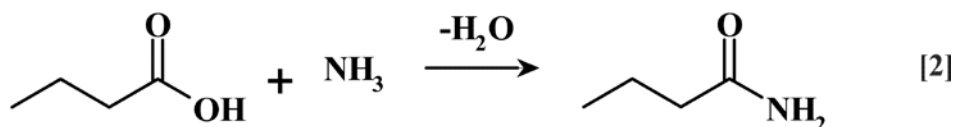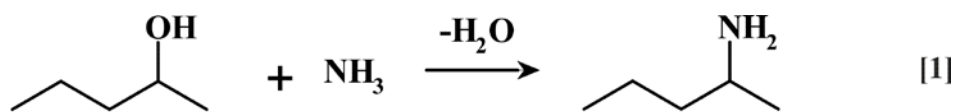
Scheme S1. Schematic representation of the formation of N-GO via NH_3 nucleophilic addition to hydroxylic, carboxylic and epoxy groups.

3.1. X-ray diffraction.
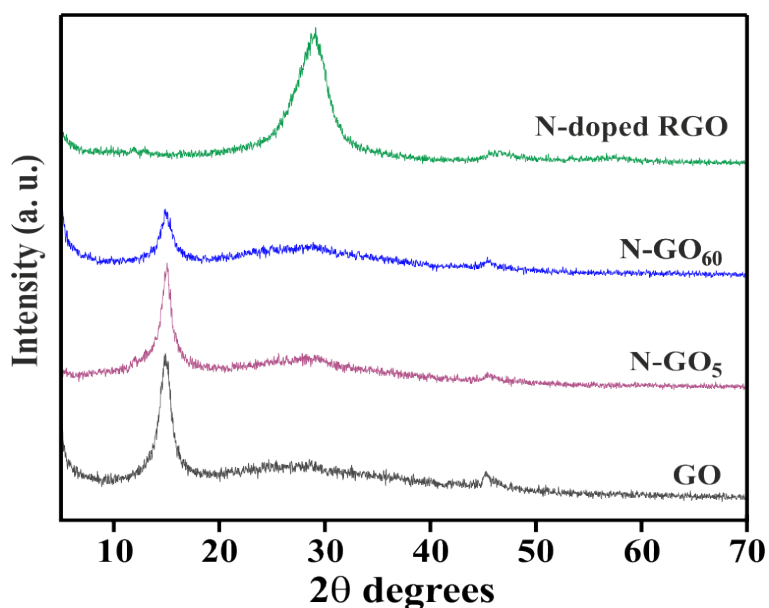
Figure S1. XRD patterns of GO and N-GO samples prepared at room temperature. A N-Doped RGO pattern is included for comparison (sample prepared by annealing GO at 500 ℃ under flowing NH_3 for 60 min, as previously reported[3]).

3.2. X-ray photoelectron analysis.
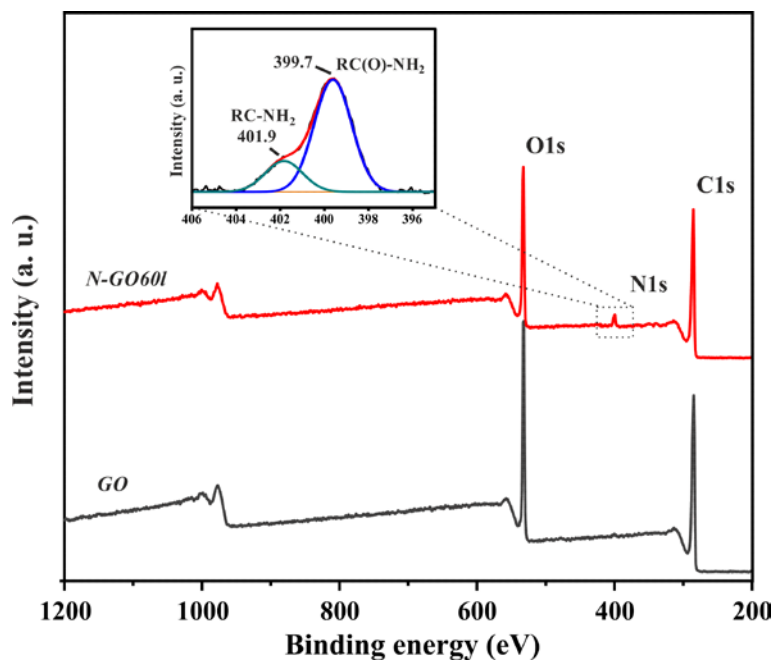
**Figure S2.** XPS general survey scan of GO and N-GO (NH_3, 60 min, 100 mL$\cdot$ min^{-1}).

X-ray photoelectron spectroscopy was employed for the detection of N within the processed samples. The deconvoluted high resolution N1s spectrum (inset Figure S1) suggests the successful functionalisation with amide (399.7 eV) and amine groups (401 eV). A shift to higher binding energies is observed if compared to signals commonly assigned to N-aliphatic functionalised GO derivatives, vibrations at BE above 401 eV usually being correlated to N atoms introduced within the conjugated network of GO. However, in some cases shifted signals have been reported for sp^3 N containing groups[4] and the additional characterisation performed in the present study allows confirming the introduction of amines and amides within the GO skeleton.

Table S2. Ratio between C, N and O species present in N-GO samples (NH$_3$ treated samples, 5-60 min) as determined by XPS analysis.

| SAMPLE NAME	Reaction time (min)	Flow of NH$_3$ (mL·min^{-1})	Carbon content (at. %)	Nitrogen content (at. %)		Oxygen content (at. %)		
				RC(O)NH$_2$	RCNH$_2$	O=C-O	O=C	O-C
GO	--	--	72.4	1.5		5.2	18.3	3.5
				0.6		27.0		
N-GO$_5$	5	300	70.9	1.5	0.8	5.0	20.3	1.5
				2.3		26.8		
N-GO$_{15}$	15	300	72.6	1.9	0.6	4.4	19.2	1.3
				2.5		24.9		
N-GO$_{30}$	30	300	71.1	2.3	0.7	4.2	20.0	1.7
				3.0		25.9		
N-GO$_{60}$	60	300	70.8	2.2	0.6	3.2	21.8	1.4
				2.8		26.4		
---	60	100	70.8	2.6	0.7	4.3	19.2	2.4
				3.3		25.9		

3.3.   Infrared spectroscopy.
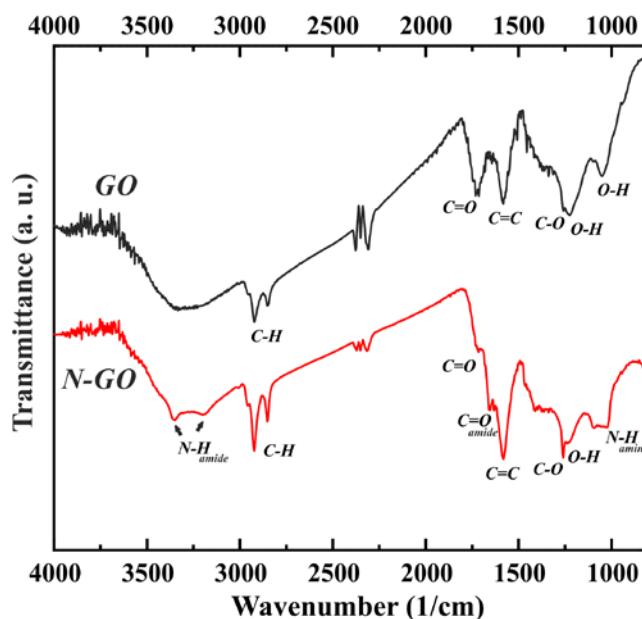
Figure S3. FT-IR of GO and ammonia treated GO at room temperature.

4. FT-IR spectroscopy was carried out in order to qualitatively determine the functional groups attached to GO after NH$_3$ treatment. The characteristic bands of O-containing aliphatic groups can be observed in the GO spectrum (Figure S2, black line). The O-H stretching vibrations (*s*O-H) from phenol and hydroxyl moieties from carboxylate fractions (*s*C=O band at 1723 cm^{-1}) are responsible of the wide band observed within the 3000-3700 cm^{-1}

range. This signal can also arise from water, easily absorbed by the GO surface. The narrow band at 1582 cm^{-1} is attributed to sC=C from the conjugated structure, while the signals at 1260 cm^{-1}, 1225 cm^{-1} and 1050 cm^{-1} are consequence of sC-O vibrations and O-H bending (bO-H) originated by hydroxyl groups closely linked to the structure. Significant changes are observed in the FT-IR spectrum of the N-functionalised sample when compared to the starting GO. Instead of the wide band at ca. 3000 cm^{-1} corresponding to free and linked O-H signals two well differentiated signals appear at 3355 cm^{-1} and 3200 cm^{-1}, resulting from sN-H present in primary amides. There is a decrease in the C=O/C=C intensity ratio, while small peaks, usually attributed to sC=O in amides and bN-H of amino groups, are observed at ca. 1650 cm^{-1}. The FT-IR spectrum also undergoes modifications at lower wavenumbers. After ammonolysis the 1225 cm^{-1} (bO-H) signal decreases as consequence of the elimination of hydroxyl groups, (replaced by -NH$_2$ moieties).[3, 5] Moreover, a new signal appears at 1094 cm^{-1} arising from C-N bonds vibrations from aliphatic amines. The above analysis confirms the successful covalent functionalisation of GO with amines and amides by NH$_3$ treatment.

5. Quantitative determination of the concentration of amine groups attached to the RGO lattice
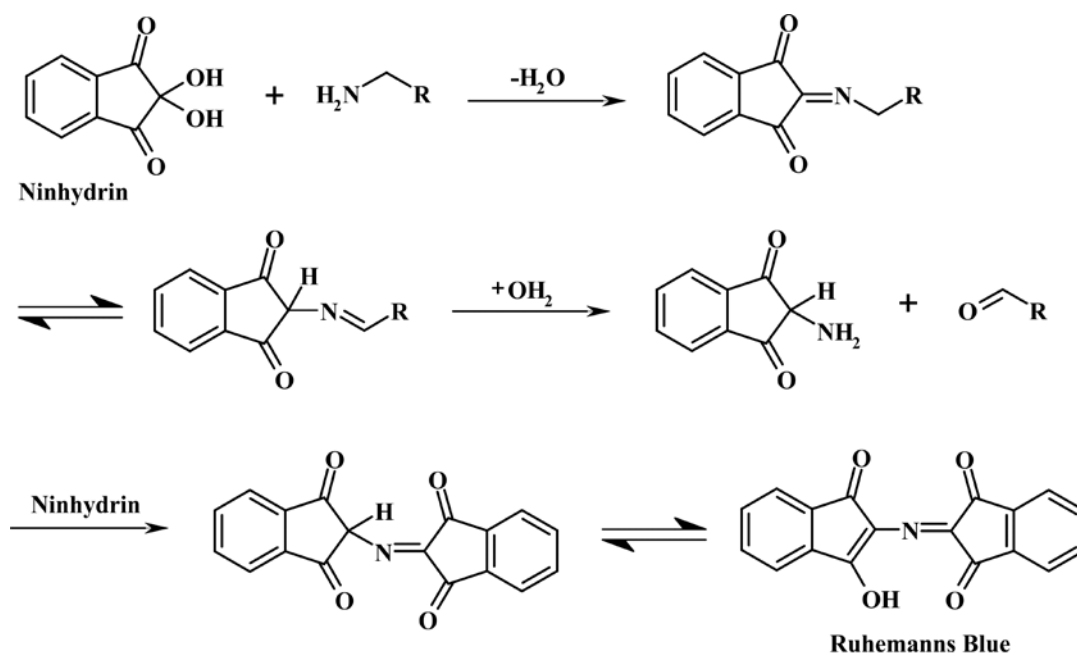
Scheme S2. Shematic representation of the formation of Ruhemanns Blue via reaction of ninhydrin with a primary amine.

|	Value	Standard Error
Intercept	-0.00325	9.48103E-4
Slope	4500.514	21.22702
Adj. R-Square	0.9999	
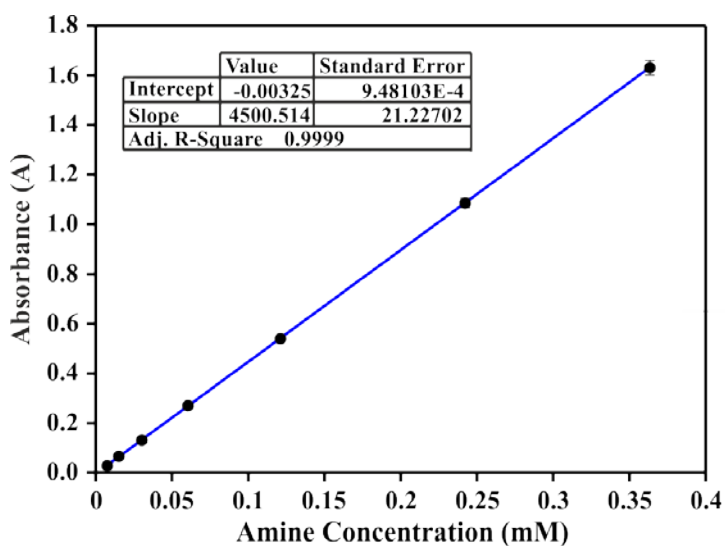
Figure S4. Calibration curve of Ruhemanns blue (RB), the reaction product of hexylamine with ninhydrin. Note that the concentration of RB is equivalent to the NH_2-loading in hexylamine.

Table S3. NH_2-loading of selected samples as determined by Kaiser test.

Sample	NH_2-loading (mmol·g^{-1})	Expected NH_2-loading (mmol·g^{-1})
Behenamide	--	--
Tentagel^{TM}-HL-NH$_2$	0.35	0.40
GO	--	--
N-doped RGO	--	--
N-GO (60 min)	0.35	0.46

6. Scanning and transmission electron microscopy study
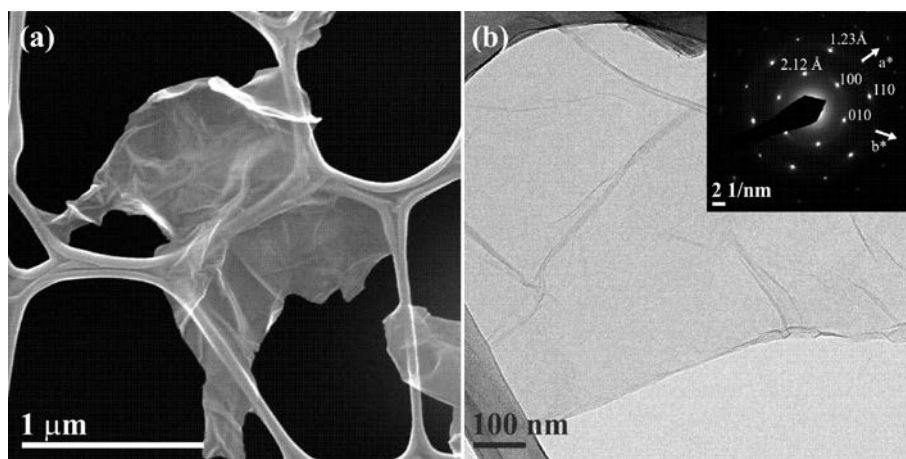
Figure S5. (a) Scanning electron microscopy (SEM) image and (b) Transmission electron microscopy (TEM) image with the corresponding SAED pattern of the N-GO$_{60}$ sample. The material was prepared by ammonolysis treatment at room temperature (time= 60 min, flow of NH$_3$, 300 mL.min^{-1}).

7. References

1   D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L. B. Alemany, W. Lu and J. M. Tour, *ACS Nano*, 2010, **4**, 4806.
2   S. Sandoval, N. Kumar, A. Sundaresan, C. N. R. Rao, A. Fuertes and G. Tobias, *Chemistry – A European Journal*, 2014, **20**, 11999.
3   S. Sandoval, N. Kumar, J. Oro-Solé, A. Sundaresan, C. N. R. Rao, A. Fuertes and G. Tobias, *Carbon*, 2016, **96**, 594.
4   M. S. Ahmed and Y.-B. Kim, *Carbon*, 2017, **111**, 577.
5   J. R. Dyer, *Applications of Absorption Spectroscopy of Organic Compounds*, Prentice Hall, New Jersey, 1965.