Electronic Supplementary Material (ESI) for Nanoscale.

Electronic Supplementary Information

Chemical reactivity of graphene oxide towards amines elucidated by solid-state NMR

Isabella A. Vacchi,[a] Cinzia Spinato,[a] Jésus Raya,[b] Alberto Bianco,[a]* and Cécilia Ménard-Moyon*[a]

---

[a] I. A. Vacchi, Dr. C. Spinato, Dr. A. Bianco, Dr. C. Ménard-Moyon
CNRS, Institut de Biologie Moléculaire et Cellulaire, Immunopathologie et Chimie Thérapeutique, 67000 Strasbourg (France)

[b] Dr. J. Raya
Membrane Biophysics and NMR, Institute of Chemistry, UMR 7177, University of Strasbourg, Strasbourg (France)

Materials and methods

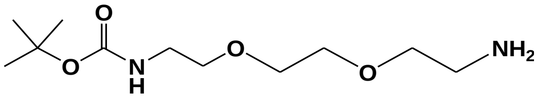
GO samples were provided by Grupo Antolin (Spain) and NanoInnova (Spain) (batch: GO.M.60-8). The chemicals and solvents were obtained from commercial suppliers and used without purification. In particular, poly(ethylene glycol) dimethyl ether (average MW 1,000) and aminopolyethylene glycol monomethyl ether (MW 1,000) were purchased from Sigma Aldrich and Alfa Aesar, respectively. The solvents used for synthesis were analytical grade. When anhydrous conditions were required, high quality commercial dry solvents were used. Water was purified using a Millipore filter system MilliQ®. When stated, suspensions were sonicated in a water bath (20 W, 40 kHz). The filtration and dialysis membranes were purchased from Millipore and Spectrum Laboratories, Inc., respectively. Thin layer chromatography (TLC) was conducted on pre-coated aluminum plates with 0.25 mm Macherey-Nagel silica gel with fluorescent indicator UV254. Chromatographic purifications were carried out with silica gel (Merck Kieselgel 60, 40-60 µm, 230-400 mesh ASTM). ^{1}H and ^{13}C-liquid-state NMR spectra were recorded in deuterated solvents using Bruker Avance I - 300 MHz and Bruker Avance III - 400 MHz. Chemical shifts are reported in ppm using the residual signal of deuterated solvent as reference. The resonance multiplicity is described as s (singlet), t (triplet), bs (broad singlet), and bt (broad triplet). Coupling constants (J) are given in Hz.

XPS was performed on a Thermo Scientific K-Alpha X-ray photoelectron spectrometer with a basic chamber pressure of 10^{-8}-10^{-9} bar and an Al anode as the X-ray source (1486 eV). The samples were analyzed as powder. Spot size of 400 µm was used. The survey spectra are average of 10 scans with a pass energy of 200.00 eV and a step size of 1 eV. The high resolution spectra are an average of 10 scans with a pass energy of 50 eV and a step size of 0.1 eV. An ion gun was turned on during analysis. For each sample the analysis was repeated three times. For the deconvolution thirty five articles on GO and XPS characterization were examined; a selection of four articles is found in references 1-4. Taking into account that the values of the binding energies of the different groups were too spread, causing overlaps and in consequence imprecision, we decided to consider the sp^2 and sp^3 carbon peaks, the hydroxyl and the epoxide, and the carbonyl and the carboxylic acid groups together, at an interval of 284.4-285.3 eV, 286.2-287.2 eV, and 287.6-289.9 eV, respectively. The C-N bond was detected at 285.4-286.0 eV, but a range of error has to be taken into consideration due to the fact that the binding energy of this bond overlaps with the C-O and the C-C areas. The full width at half maximum (FWHM) was kept constant for each curve, except for the C-N bond that was kept lower because it is a signal of a single group. We did not perform a shift correction to avoid adding a user error. For the deconvolution CasaXPS program was used. Elemental analyses were carried out by combustion using Flash 2000 apparatus from Thermo Fisher Scientific. TGA was performed on a TGA1 (Mettler Toledo) apparatus from 30 °C to 900 °C with a ramp of 10 °C·min^{-1} under N_2 using a flow rate of 50 mL·min^{-1} and platinum pans. FT-IR spectra were measured on a Perkin Elmer Spectrum One ATR-FT-IR spectrometer. Raman spectroscopy was performed using a Renishaw inVia microRaman equipped with a Leica microscope. The spectra were recorded using 514 nm laser (5% laser power) and ×50 objective lens. The samples were prepared by drop casting water dispersions of the respective samples on Si window -E coated (Ø25.4 mm, 5 mm thick) substrates (ThorLabs), followed by drying at room temperature. TEM analysis was performed on a Hitachi H600 or on a Hitachi H7500 microscope with an accelerating voltage of 75 kV or 80 kV, respectively. The samples were dispersed in water/MeOH (1:1) at a concentration of 0.05 mg·mL^{-1} and the suspensions were sonicated for 15 min. Ten microliters of the suspensions were drop-casted onto a carbon-coated copper grid (Formvar/Carbon 300 Mesh, Cu from Delta Microscopies) and left for evaporation under ambient conditions. Solid-state MAS NMR experiments were performed on an AVANCE 750 MHz wide bore spectrometer (BrukerTM) operating at a frequency of 188.5 MHz for ^{13}C and equipped with two different MAS probes: a double resonance MAS probe designed for 2.5 mm o.d. zirconia rotors (closed with Kel-F caps) and a triple resonance MAS probe designed for 3.2 mm zirconia rotors (also closed with Kel-F caps). The samples were spun either at 30 kHz spinning frequency (MAS 2.5) for GO-N or 18 kHz (MAS 3.2) for GO-A, GO-N **2**, and GO-A **2**. 2D ^{1}H-^{13}C HETCOR with FSLG irradiation during the evolution time[5] was obtained with the first CP step following the Adiabatic Passage through the Hartmann-Hahn (HH) conditions scheme.[6] The latter conditions were set to 97 kHz and 127 kHz B1 fields for ^{13}C and ^{1}H, respectively (when spinning at 30 kHz), and 90 kHz /108 kHz in the other case (MAS = 18 kHz). The ^{1}H RF field was swept from 107 to 147 kHz (MAS = 30 kHz) or from 93 kHz to 123 kHz (MAS = 18 kHz) through the HH condition using the tangential time dependence and defined by the shape angle $\phi = at_{cp}/2$ where a is the rate of angular,[7] ϕ and t_{cp} (contact time) were set to 88° and 1.5 ms after optimization.[8] Proton decoupling during acquisition was obtained by using SPINAL-64[9] at a 180 kHz RF field (for both probes), while the recycle time was set to 1 s. The duration of the successive FSLG pulses was 3.57 µs and the magic-angle pulse length was 1.34 µs. A number of 192 complex data points were acquired in the ^{1}H indirect dimension and for each t1 increment 2048 scans were accumulated leading to a time resolution of 6.3361 ms for ^{1}H and 12.2880 ms for ^{13}C. Prior to Fourier transformation, a Lorentzian line broadening of 150 Hz was applied in the direct dimension while the proton dimension apodization was done with a 90° shifted squared sine-bell function.

1D ^{13}C{^{1}H} CP/MAS spectra were recorded with the same spectral parameters than 2D spectra. But, owing to the spectral wide lines and in order to get undistorted lineshapes, we used and improved CP experiment version that perform Hahn's echo prior to FID acquisition.[10] The latter echo had to be synchronized with the rotation (echo time = n rotation periods) and was kept identical for all ^{13}C spectra and equal to two rotation periods. The total echo time was 66.67 µs (MAS = 30 kHz) and 111.11 µs (MAS = 18 kHz).

Quantitative 1D $^{13}C\{^1H\}$ DP spectra were acquired directly with the original Hahn's echo sequence,[10] with a recycling delay set to 30 s to ensure reliable quantitation (total experimental time was 24 h per spectrum).

Preparation of {2-[2-(2-amino-ethoxy)-ethoxy]-ethyl}-carbamic acid *tert*-butyl ester 1



To a solution of 2,2'-(ethylenedioxy)bis(ethylamine) (9.85 mL, 67.5 mmol) in CH_2Cl_2 (15 mL) in an ice bath, was added a solution of Boc_2O (2.94 g, 13.5 mmol) in CH_2Cl_2 (45 mL) dropwise over a period of 3 h. The reaction mixture was stirred overnight at room temperature. The solvent was removed under reduced pressure. After dissolving the residue in H_2O (200 mL), the precipitate formed was filtered on celite. The filtrate was extracted with CH_2Cl_2 (100 mL x 3) and dried over Na_2SO_4. Evaporation of the solvent *in vacuo* afforded compound **1** as colorless oil (2.85 g, 11.5 mmol, 85%). NMR spectroscopy showed a satisfactory purity; therefore the crude was used without purification.

^1H NMR (300 MHz, $CDCl_3$): δ= 5.13 (*bs*, 1H, NH), 3.60 (*s*, 4H, CH_2), 3.53 (*t*, 5.1 Hz, 4H, CH_2), 3.30 (*bt*, 2H, CH_2), 2.89 (*t*, 5.1 Hz, 2H, CH_2), 2.20 (*s*, 2H, CH_2), 1.42 ppm (*s*, 9H, *t*Bu). ^{13}C NMR (75 MHz, $CDCl_3$): δ= 155.9, 78.8, 73.1, 70.0, 41.5, 40.2, 28.3 ppm.

All structural assignments were in agreement with the data available from the literature.[11]

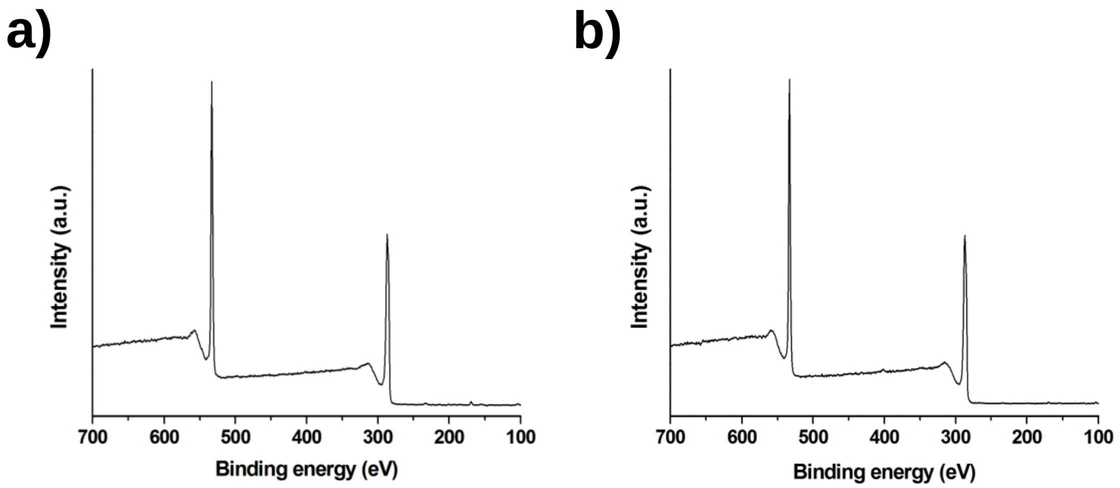


Figure S1. XPS of GO-N (a) and GO-A (b).

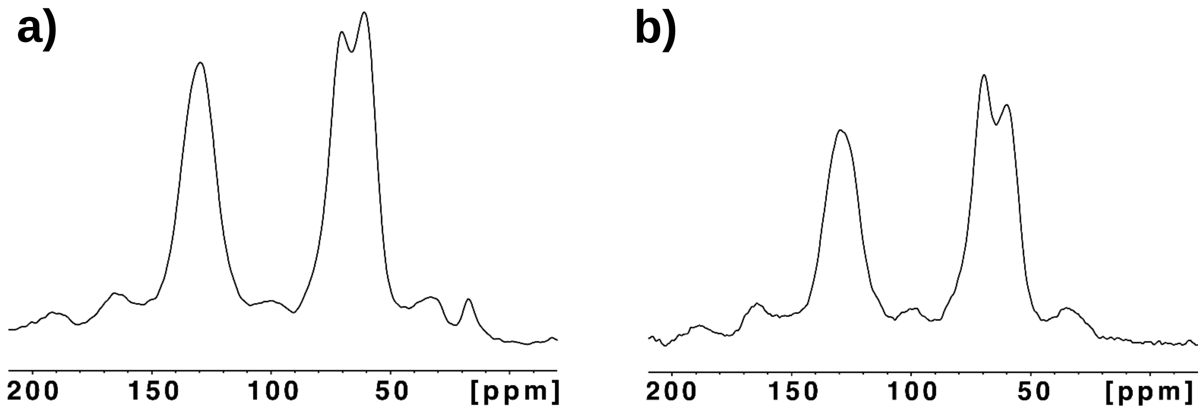


Figure S2. Quantitative ^{13}C NMR spectra of GO-N (a) and GO-A (b).

a)

δ (ppm)	%
16.5	3.8
58.9	29.7
69.7	30.5
102.2	2.4
129.3	30.2
189.6	3.5

b)

δ (ppm)	%
59.1	15.3
69.8	34.1
97.6	5.3
128.3	42.9
186.8	2.5

Table S1. Percentages of the different peaks for GO-N (a) and GO-A (b) obtained from the quantitative ^{13}C NMR spectra. The chemical shift assigned to carbonyls is in red.

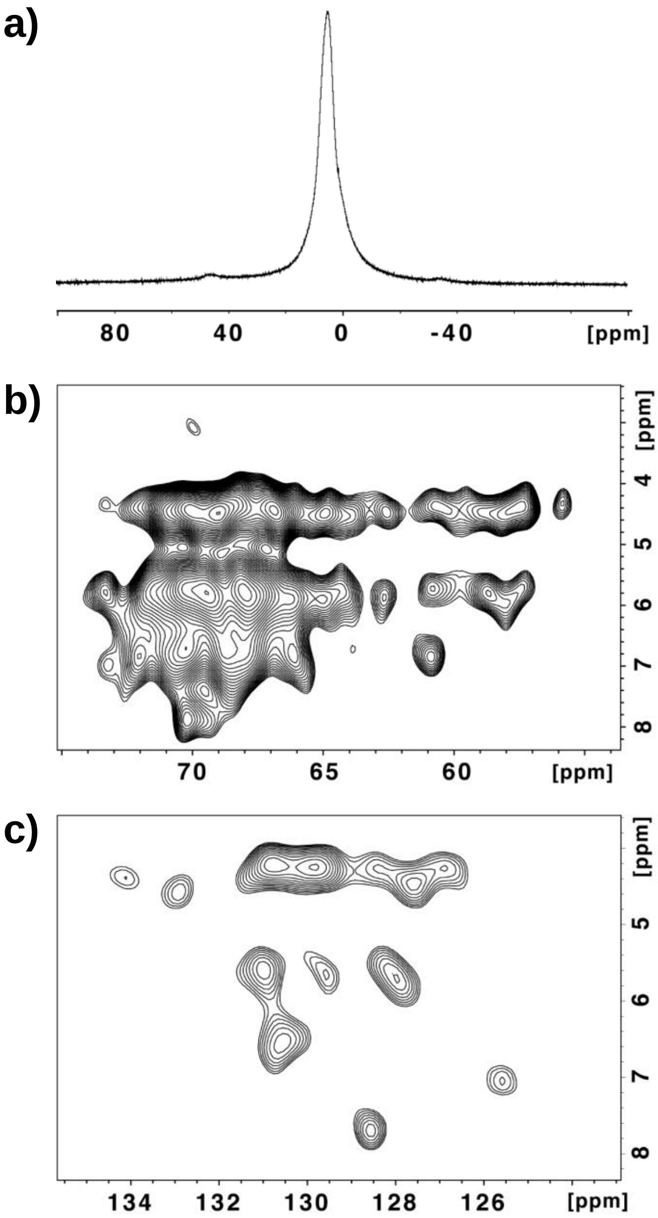


Figure S3. ^{1}H NMR (a) and magnified ^{1}H-^{13}C correlation (b, c) spectra of GO-N.

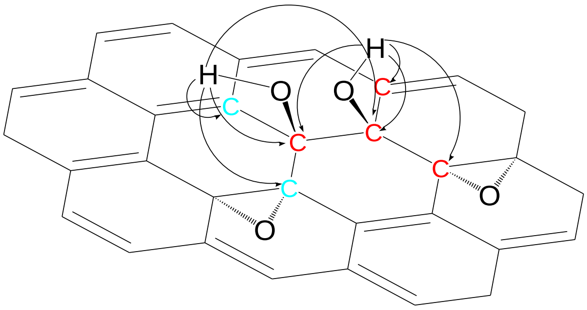


Figure S4. Tentative chemical structure of GO-N based on the chemical shifts of the protons that cross-correlate with carbons on the same graphene sheet. The protons of the OH groups that are between 4.5 and 7.5 ppm can generate cross-peaks with the carbon in the aliphatic (55-70 ppm) and aromatic regions (125-135 ppm). Interlayer spatial interactions are also possible.

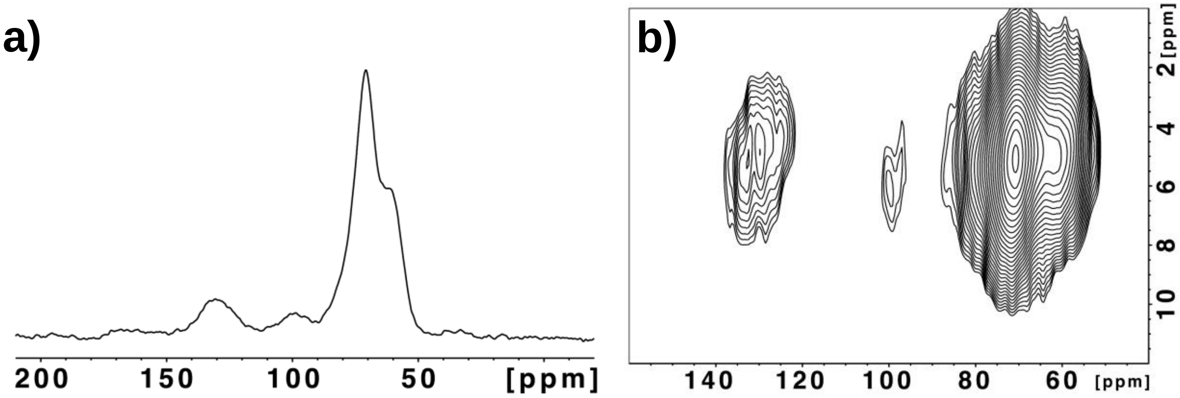
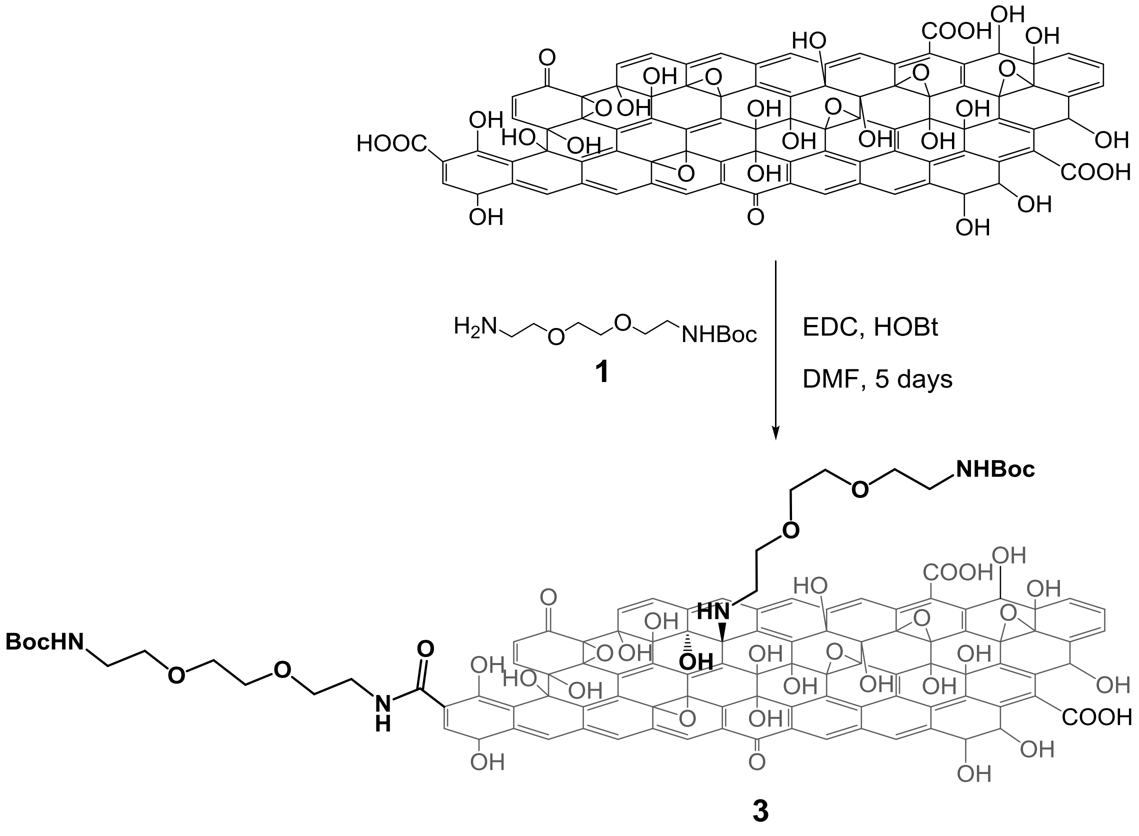


Figure S5. ^{13}C NMR (a) and ^{1}H-^{13}C correlation (b) spectra of GO-A.



Scheme S1. Concomitant amidation and nucleophilic epoxide opening of GO by TEG diamine derivative **1**. For the sake of clarity, only one carboxylic group and one epoxide are derivatized.

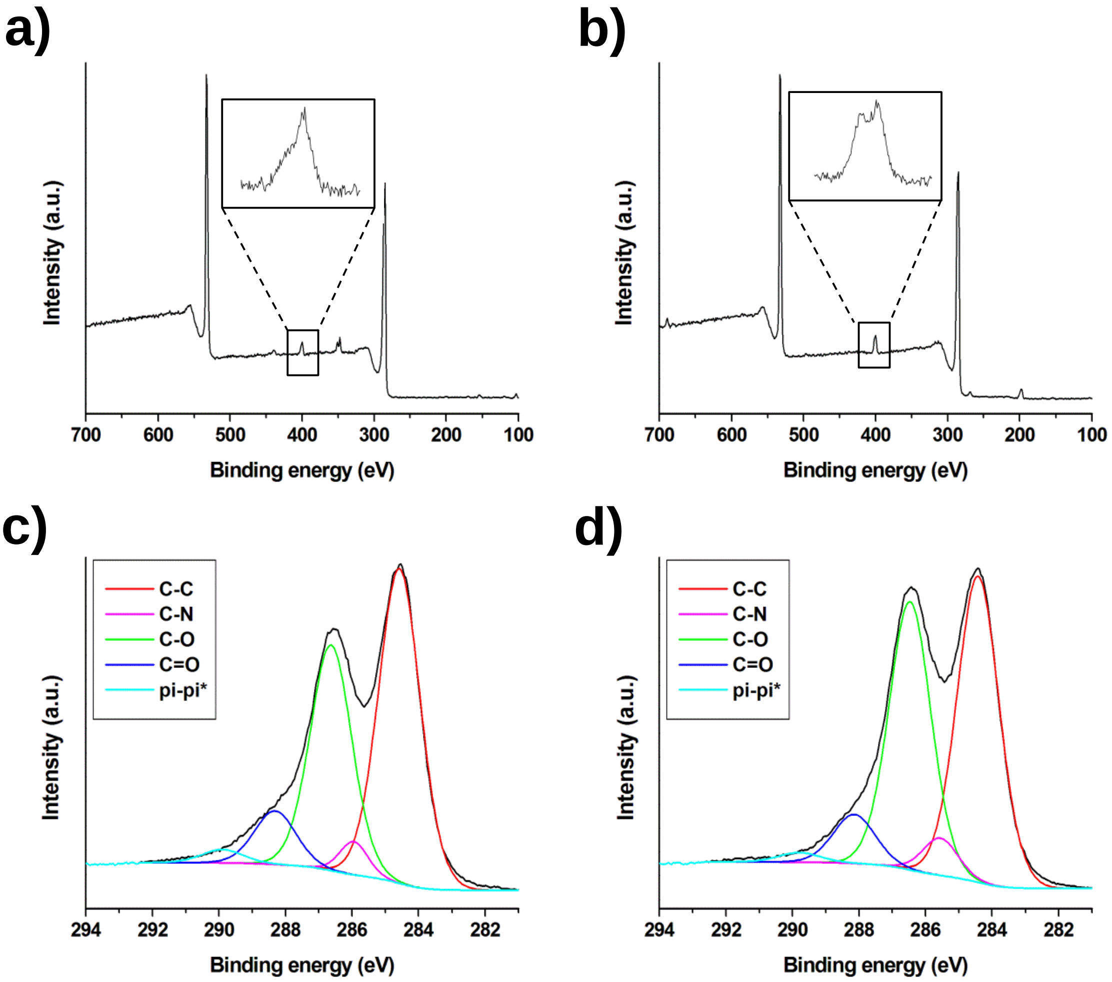


Figure S6. XPS of GO-A **2** (a) and **3** (b) with a zoom on the N (1s) peak. Deconvolution of the C (1s) peak for GO-A **2** (c) and GO-A **3** (d).

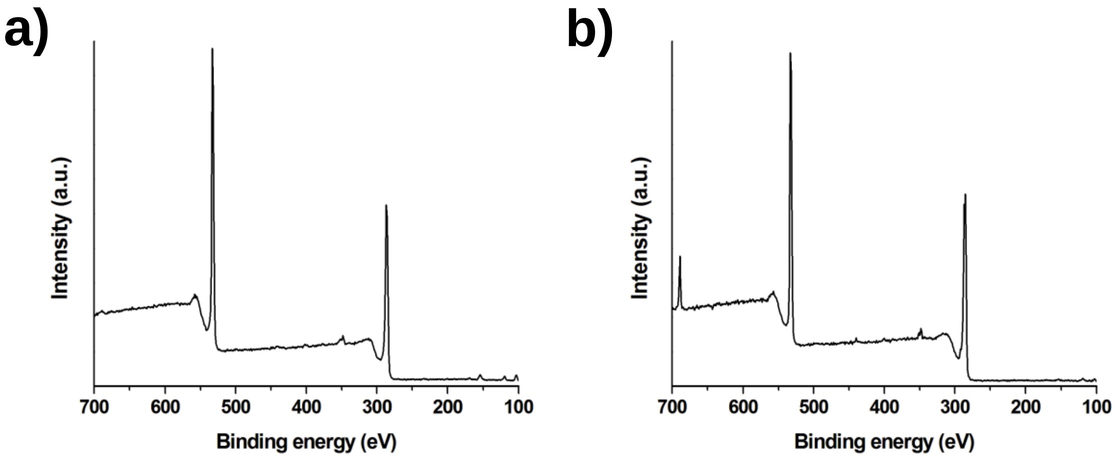


Figure S7. XPS of GO-N CONT (a) and GO-A CONT (b).

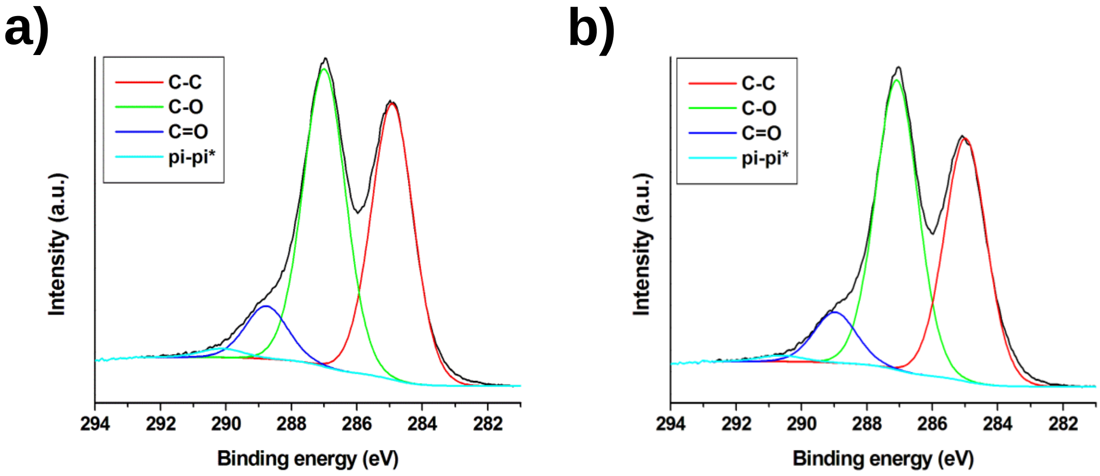
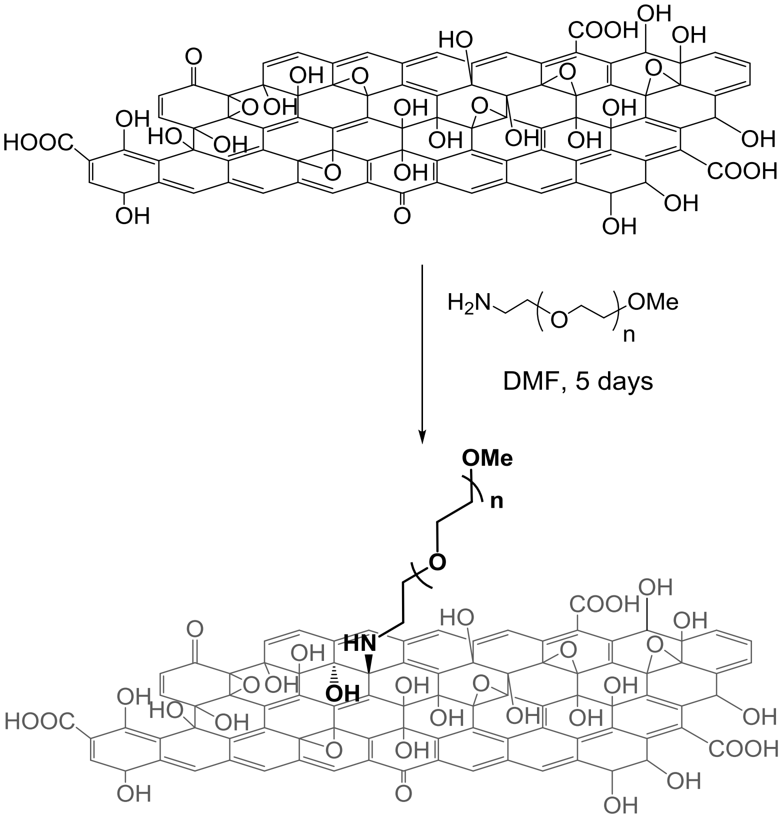
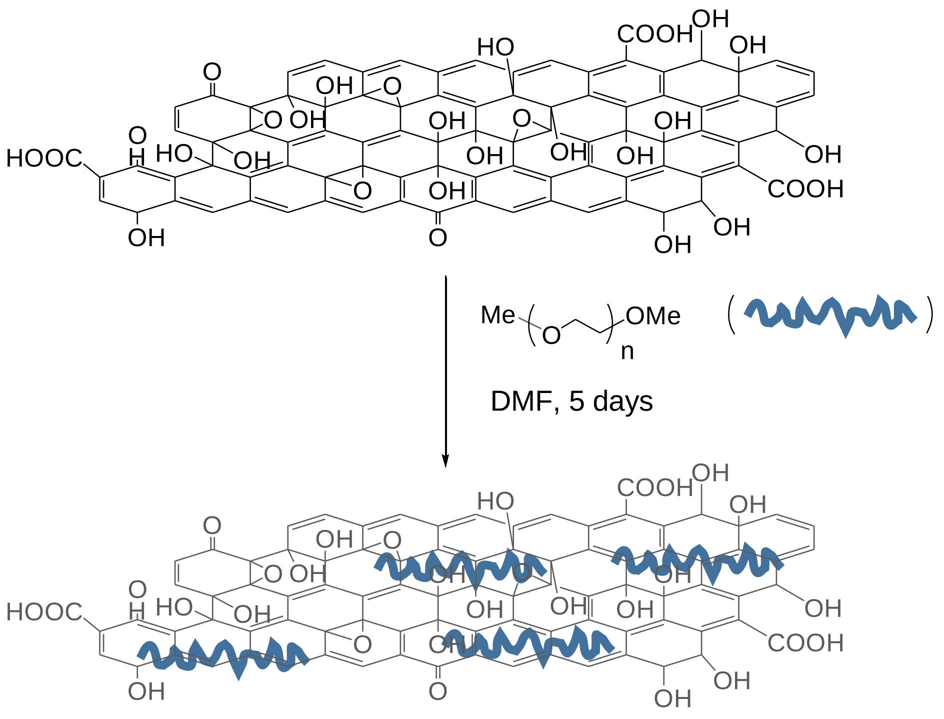


Figure S8. Deconvolution of the C (1s) peak for GO-N (a) and GO-A (b).



4

Scheme S2. Derivatization of GO-N with aminopolyethylene glycol monomethyl ether (average MW 1,000).



5

Scheme S3. Control reaction by mixing GO-N and poly(ethylene glycol) dimethyl ether (MW 1,000) to assess the capacity of PEG to adsorb on GO-N. The PEG derivative is represented by the blue curved line.

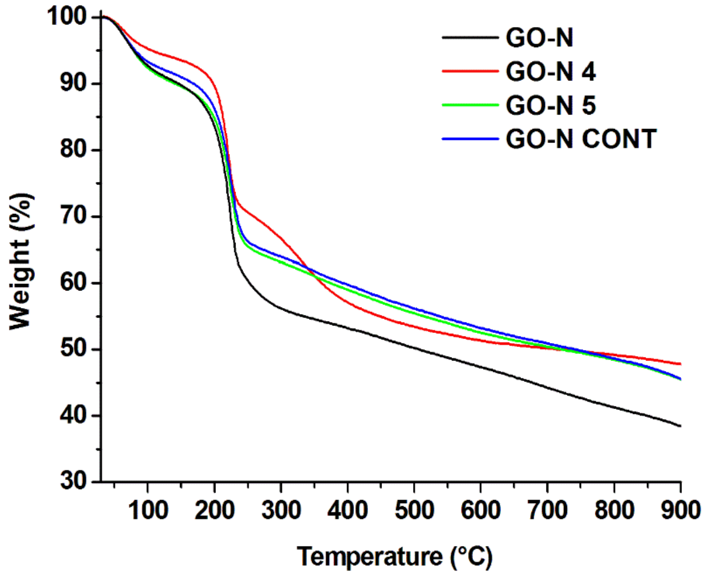


Figure S9. TGA of GO-N, GO-N **4**, GO-N **5**, and GO-N CONT in inert atmosphere.

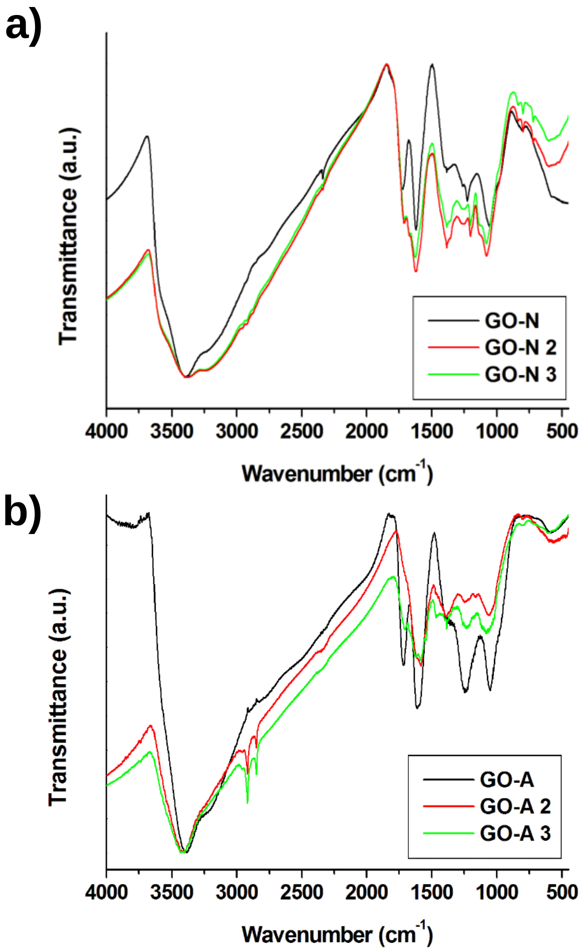


Figure S10. FT-IR spectra of GO, GO **2**, and GO **3** for the NanoInnova (a) and Antolin (b) materials.

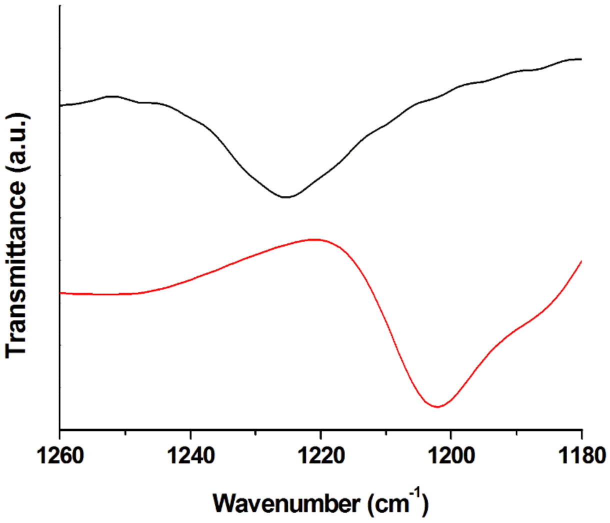


Figure S11. Zoom on the FT-IR spectra of GO-N (black) and GO-N **2** (red).

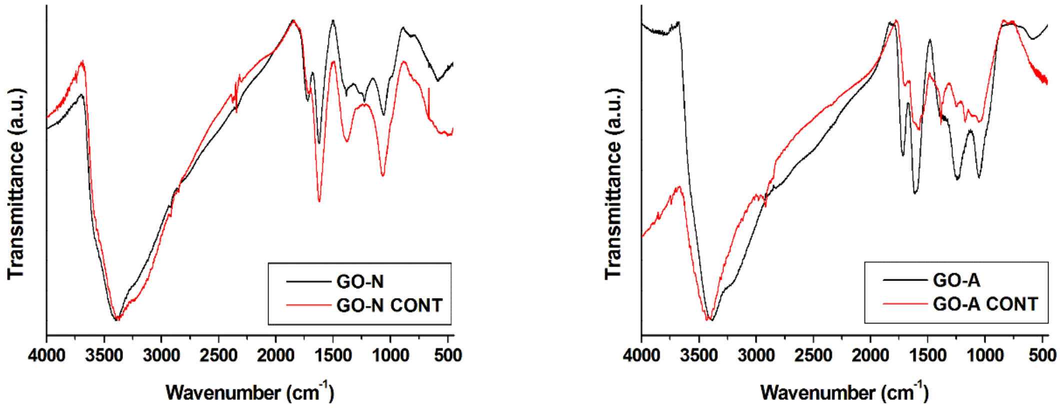


Figure S12. FT-IR spectra of GO and control treated GO sample for the NanoInnova (left) and Antolin (right) materials.

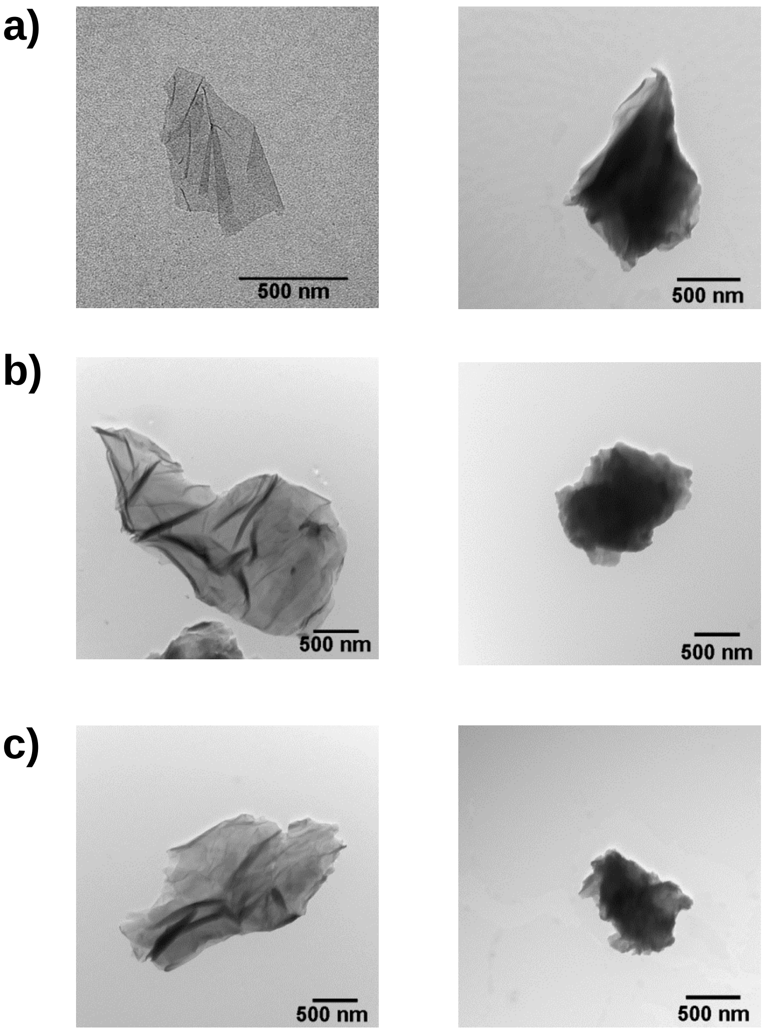


Figure S13. TEM images of GO (a), GO **2** (b), and GO **3** (c) for the NanoInnova (left) and Antolin (right) materials.

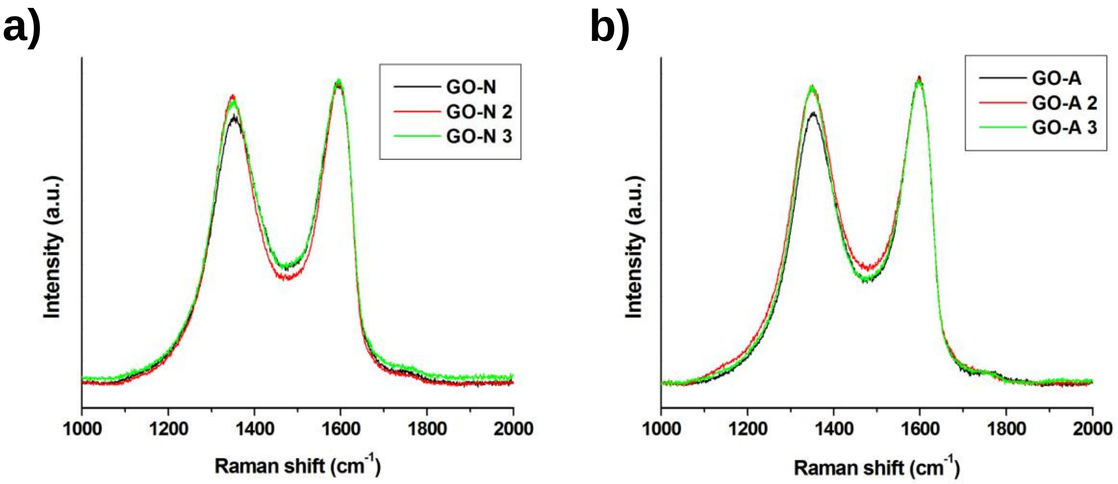


Figure S14. Raman spectra of GO, GO **2**, and GO **3** for the NanoInnova (a) and Antolin (b) materials. The spectra were normalized to the G band intensity.

References

1 A. Navaee and A. Salimi, *RSC Adv.*, 2015, **5**, 59874–59880.

2 W. Tong, Y. Zhang, Q. Zhang, X. Luan, Y. Duan, S. Pan, F. Lv and Q. An, *Carbon*, 2015, **94**, 590–598.

3 A. Ejigu, M. Edwards and D. A. Walsh, *ACS Catal.*, 2015, **5**, 7122–7130.

4 Y. Xue, Y. Liu, F. Lu, J. Qu, H. Chen and L. Dai, *J. Phys. Chem. Lett.*, 2012, **3**, 1607–1612.

5 B.-J. van Rossum, H. Förster and H. J. M. de Groot, *J. Magn. Reson.* 1997, **124**, 516–519.

6 T. Egorova-Zachernyuk, B. van Rossum, C. Erkelens and H. de Groot, *Magn. Reson. Chem.* 2008, **46**, 1074–1083.

7 S. Hediger, B. H. Meier, N. D. Kurur, G. Bodenhausen and R. R. Ernst, *Chem. Phys. Lett.* 1994, **223**, 283–288.

8 J. Raya, B. Perrone, J. Hirschinger, *J. Magn. Reson.* 2013, **227**, 93–102.

9 B. M. Fung, A. K. Khitrin and K. Ermolaev, *J. Magn. Reson.* 2000, **142**, 97–101.

10 E. L. Hahn, *Phys. Rev.* 1950, **80**, 580–594.

11 G. Pastorin, W. Wu, S. Wieckowski, J.-P. Briand, K. Kostarelos, M. Prato and A. Bianco, *Chem. Commun.* 2006, 1182–1184.