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Is carboxylation an efficient method for graphene oxide functionalization?

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Electronic Supplementary Information

Materials and methods

All the chemicals and solvents were obtained from commercial suppliers and used without purification. *O*-(2-aminoethyl)-*O′*-[2-(Boc-amino)ethyl]decaethylene glycol (BocNH-PEG_{10}-NH_2) was purchased from Polypure AS. The solvents used during the reaction were analytical grade. Water was purified by a Millipore filter system MilliQ®. GO suspensions were prepared by sonication in a water bath (20 W, 40 kHz) with a controlled temperature between 20°C and 30°C. For dialysis, MWCO 12,000-14,000 Da membranes were purchased from Spectrum Laboratories, Inc. Thermogravimetric analysis (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 atmosphere with a flow rate of 50 mL·min^{-1} and platinum pans. Transmission electron microscopy (TEM) analysis was performed on a Hitachi H600 with an accelerating voltage of 75 kV. The samples were dispersed in water/ethanol (1:1) at a concentration of 16 μg·mL^{-1} and the suspensions were sonicated for 10 min. Ten microliters of the suspensions were drop-casted onto a copper grid (Formvar film 300 Mesh, Cu from Electron Microscopy Sciences) and left for evaporation under ambient conditions. Attenuated total reflectance (ATR)-FTIR was performed using a Thermo Scientific Nicolet™ 6700 FT-IR spectrometer equipped with an ATR accessory (diamond ATR polarization accessory with 1 reflection top-plate and pressure arm). The pressure arm was used for all solid samples at a force gauge setting between 100 and 120 units. The number of scans was set at 30. Samples were loaded on the reflection top-plate at a quantity sufficient enough to cover the entire diamond surface. ^{1}H liquid-state NMR spectra were recorded in deuterated solvents using Bruker Avance I - 300 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), dd (doublet of doublet), dt (doublet of triplet). Coupling constants (J) are given in Hz.

The X-ray photoelectron spectroscopy (XPS) experiments were performed on a Thermo Scientific KAlpha 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 pressed onto a scotch tape (3MTM EMI Copper Foil Shielding Tape 118). Spot size of 400 μm was used for analysis. The survey spectra are an 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. The pass energy of 50.00 eV corresponds to Ag $3d_{5/2}$ full width line at half maximum (FWHM) of 1.3 eV. A pass energy of 50.00 eV for the high resolution spectra was applied because lower pass energies have shown no improvement in FWHM for graphene materials on Thermo Scientific K-ALPHA.[1] For each sample, the analysis was repeated three times. A flood gun was turned on during analysis. We grouped the functional groups of C 1s spectra to avoid imprecision due to the proximity of the peak values, since the binding energy values in the literature were too spread. Therefore, the C 1s spectra were deconvoluted in C=OOH (288.7-289.1 eV) for carboxyl groups, C=O (288.1-288.3eV) for carbonyl groups, C-O (286.2-287.2 eV) for hydroxyls and epoxides and C-C (284.4-285.3 eV) for sp^2 and sp^3 carbon atoms. For data analysis, the software casaXPS (2.3.18) was used. A Shirley background subtraction was applied. A line-shape 70% Gaussian/30% Lorenzian [GL(30)] was selected for all peaks. The full width at half maximum was constrained to be the same for all peaks, apart for the pi-pi* peak because it is a broad signal. Similarly, the O 1s spectra were deconvoluted in C=O (531.4-530.3 eV), C-O (533.0-532.0 eV) and H_2O (535.2-534.8 eV).

^{13}C solid-state NMR experiments were performed at room temperature on an AVANCE 300 MHz wide-bore spectrometer (Bruker™) operating at a frequency of 75.52 MHz for ^{13}C. All the samples were spun at 12 kHz in a double resonance MAS (Magic Angle Spinning) probe designed for 4 mm

o.d. zirconia rotors (closed with Kel-F caps). All spectra were acquired following the Hahn's spin-echo experiment pulse scheme[3] as it allows to get undistorted line shapes and flat baselines that are prerequisites for quantitative analysis. Echo times were synchronized with the rotation (echo time = 2 rotation periods = 166.67 μs) and durations were 2.73 μs and 5.46 μs for π/2 and π pulses respectively. Proton decoupling during acquisition was done using SPINAL-64 decoupling[4] at a 73 kHz RF field. Spectral width was set to 50 kHz and 65536 transients per FID were acquired on 8192 time domain points except for pristine GO where only 7168 transients per FID were added. In order to achieve quantitative results a series of longitudinal relaxation times (T1) measurements were carried out (Inversion-Recovery method, data not shown). With the longest T1 being below 300 ms we could safely use a recycling delay of 2 s for all spin-echoes experiments. Together with a relatively high amount of sample inside the rotors (80 μL active volume) it allowed to get rather noiseless spectra in a reasonable time (ca. 12 h). A 150 Hz Lorentzian filter was applied prior to Fourier transform without zero filling. Chemical shifts were given respective to tetramethysilane (TMS) using adamantane as a secondary reference. Spectral deconvolutions were obtained using the solid line shape analysis tool (SOLA) inside the TopSpin 4.0.8 software (Bruker™). Here the CSA (Chemical Shift Anisotropy) subroutine was employed in order to get intensities (Table S1) for the minimal set of 10 sites needed to get a rather good agreement between experimental and synthetic spectra (lower traces in Figure S4 correspond to their difference).

***tert-Butyl (2-(2-(2-aminoethoxy)ethoxy)ethyl)carbamate* (Boc-TEG-NH_2)**

To a cooled solution (0°C) of 30.0 g (202.5 mmol) 2,2'-(ethylenedioxy)bis(ethylamine) in 200 mL of chloroform, a solution of 4.425 g (20.3 mmol) di-*tert*-butyl dicarbonate in 200 mL of chloroform was added dropwise under inert atmosphere. After complete addition after 2 h, the water-ice bath was removed and the mixture was allowed to warm to room temperature and it was stirred for 24 h. The organic solvent was removed under vacuum to give 4.5 g of a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.13 (s, 1H), 3.57 (s, 4H), 3.48 (dt, J = 9.3, 5.2 Hz, 4H), 3.26 (dd, J = 10.4, 5.3 Hz, 2H), 2.82 (t, J = 5.2 Hz, 2H), 1.39 (s, 9H) ppm. The ^{1}H NMR data were consistent with a previous work.[2]

Preparation of GO

A stirred suspension of graphite (3 g) in 95 wt% H_2SO_4 (75 mL) was gradually treated with the required amount of $KMnO_4$ (12 g) while keeping the temperature below 10°C, and the obtained mixture was stirred at 35°C for 2 h and then diluted with water (75 mL) under vigorous stirring. The resulting suspension was treated with 30 wt% H_2O_2 (7.5 mL), and the solids were separated and purified via repeated centrifugation and resuspension in water. The concentration of GO dispersion was adjusted to 1 wt%, then subjected to wet jet mill (0.1 mm nozzle) at 150 MPa.

Preparation of GO 1

1.2 g of sodium hydroxide was dissolved in 6 mL of water using a water bath sonication. 4 mL of GO suspension at a concentration of 5 $mg \cdot mL^{-1}$ was added to the NaOH solution. 1 g of chloroacetic acid were immediately added to the mixture and the suspension was bath sonicated for 2 h with a controlled temperature between 16 and 30°C. The mixture was then stirred at room temperature overnight and filtered over a polytetrafluoroethylene (PTFE) Millipore® membrane with 0.1 μm pore size. The GO on the membrane was collected and dispersed in water, sonicated in a water bath and filtered again. This sequence was repeated 3 times with water and 3 times with methanol. The resulting solid was

dispersed in water and the suspension was dialyzed in water for 3 days. After lyophilization, GO **1** was obtained.

Preparation of GO 2

To a suspension of GO (50 mg) in 50 mL of water, 100 mg of Boc-PEG_{10}-NH_2 was added to the solution and bath sonicated for 10 min. The mixture was then stirred at room temperature for 3 days and filtered over a PTFE filter membrane with 0.1 μm pore size. The solid on membrane was collected and washed with water and methanol for 3 times each. The solid was dispersed in water, the suspension was dialyzed in water for 3 days, and lyophilized to obtain GO **2**.

Preparation of GO 3

The preparation of GO **3** was similar to the preparation of GO **1**. Briefly, 1.8 g of sodium hydroxide was dissolved in 15 mL of water using water bath sonication. Then, 30 mg of GO **2** was added to the NaOH solution, followed by the immediate addition of 1.5 g of chloroacetic acid. The suspension was bath sonicated for 2 h with a controlled temperature below 30℃. The mixture was then stirred at room temperature overnight, filtered over a PTFE membrane, and washed with water and methanol for 3 times each. The solid was dispersed in water, the suspension was dialyzed in water for 3 days and lyophilized to obtain GO **3**.

Preparation of GO 4

To a suspension of GO **3** (10 mg) in 10 mL DMF, 3.8 mg of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC) were added. The suspension was stirred for 30 min. Then 5.8 mg of *N*-hydroxysuccinimide (NHS) were added. After stirring for 30 min, 20 mg of Boc-PEG_{10}-NH_2 were added and the suspension was bath sonicated for 10 min. The mixture was then stirred under argon atmosphere at room temperature overnight and filtered over a PTFE filter membrane with 0.1 μm pore size. The solid on membrane was collected and washed with water and methanol for 3 times each. The solid was dispersed in water, the suspension was dialyzed in water for 3 days and lyophilized to obtain GO **4**.

Preparation of GO 4-CTR

To a suspension of GO **2** (10 mg) in 10 mL DMF, 3.8 mg of EDC were added. The suspension was stirred for 30 min. Then, 5.8 mg of NHS were added. After stirring for 30 min, 20 mg of Boc-PEG_{10}-NH_2 were added and the suspension was bath sonicated for 10 min. The mixture was then stirred under argon atmosphere at room temperature overnight and filtered over a PTFE filter membrane with 0.1 μm pore size. The solid on membrane was collected and washed with water and methanol for 3 times each. The solid was dispersed in water, the suspension was dialyzed in water for 3 days and lyophilized to obtain GO **4-CTR**.

Preparation of GO 5a and GO 5b

The preparation of GO **5a** and GO **5b** is similar to GO **1**. Briefly, two different concentrations of NaOH solution was prepared (pH=9 for GO **5a**, and pH=13 GO **5b**). 6 mL of GO suspension at a concentration of 5 $mg \cdot mL^{-1}$ were added to 9 mL NaOH solution. 3 g of chloroacetic acid were immediately added and the suspension was bath sonicated for 10 min with a controlled temperature below 30℃. The mixture was then stirred at room temperature overnight, filtered over a PTFE membrane, and washed

with water and methanol for 3 times each. The solid was dispersed in water, the suspension was dialyzed in water for 3 days and lyophilized, obtaining GO **5a** and GO **5b**.

Preparation of GO 6a and GO 6b

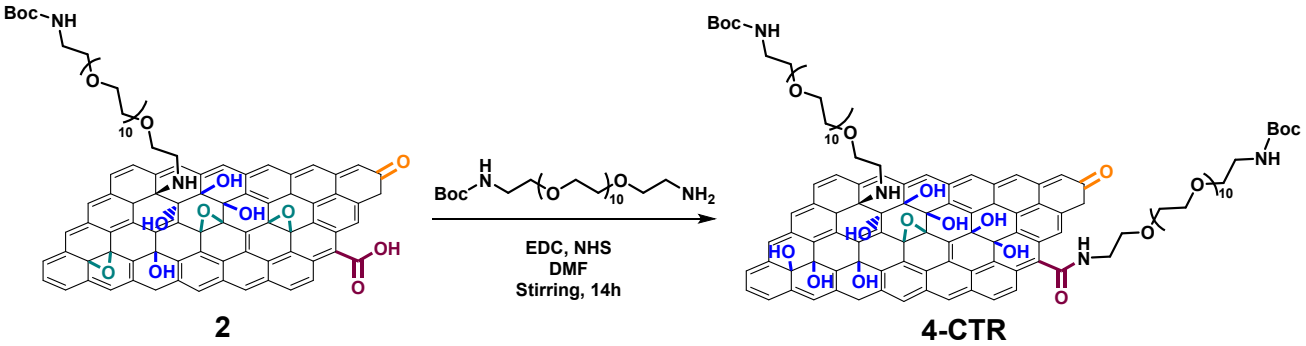
To a suspension of GO **5a** (20 mg) in 20 mL of water, 40 mg of Boc-TEG-NH_2 were added to the solution. The suspension was bath sonicated for 10 min, stirred at room temperature for 3 days, and filtered over a PTFE filter membrane with 0.1 µm pore size. The solid on membrane was collected and washed with water and methanol for 3 times each. The solid was dispersed in water, the suspension was dialyzed in water for 3 days and lyophilized to obtain GO **6a**. The preparation of GO **6b** was similar starting from GO **5b**.

Preparation of GO 7a and GO 7b

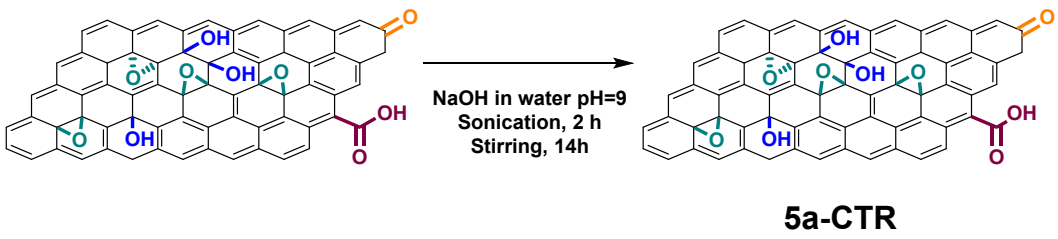
To a suspension of GO **6a** (10 mg) in 10 mL of DMF, 3.8 mg of EDC were added. The suspension was stirred for 30 min. Then, 5.8 mg of NHS were added. After stirring for 30 min, 20 mg of Boc-TEG-NH_2 were added and the suspension was bath sonicated for 10 min. The mixture was then stirred under argon atmosphere at room temperature for 3 days and filtered over a PTFE filter membrane with 0.1 µm pore size. The solid on membrane was collected and washed with water and methanol for 3 times each. The solid was dispersed in water, the suspension was dialyzed in water for 3 days and lyophilized to obtain GO **7a**. The preparation of GO **7b** was similar starting from GO **6b**.

Preparation of GO 5-CTR

GO **5a-CTR** was obtained following the protocol for the preparation of GO **5a** without adding chloroacetic acid.



Scheme S1. Preparation of control sample GO **4-CTR**.



Scheme S2. Preparation of control sample GO **5a-CTR**.

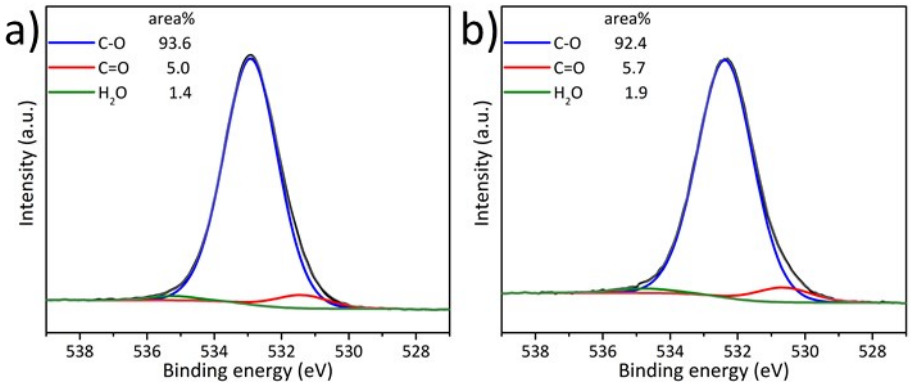


Figure S1. high resolution O 1s spectra of a) pristine GO and b) GO **1**

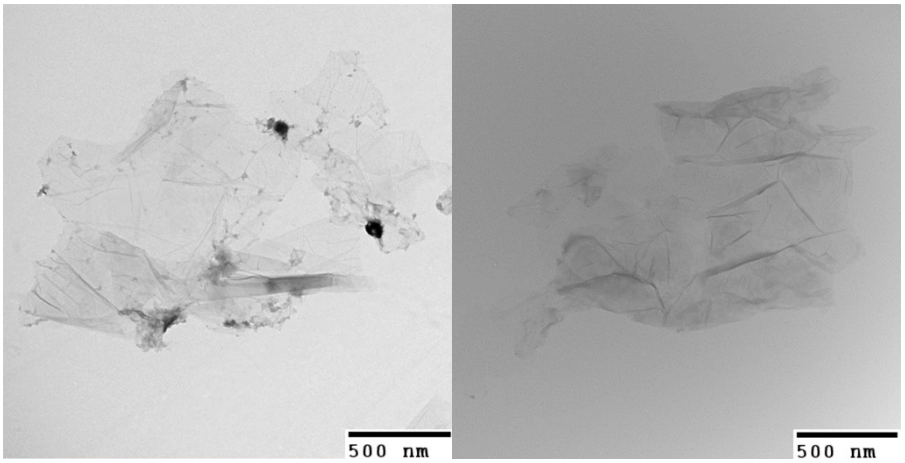


Figure S2. TEM images of GO (left) and GO **1** (right).

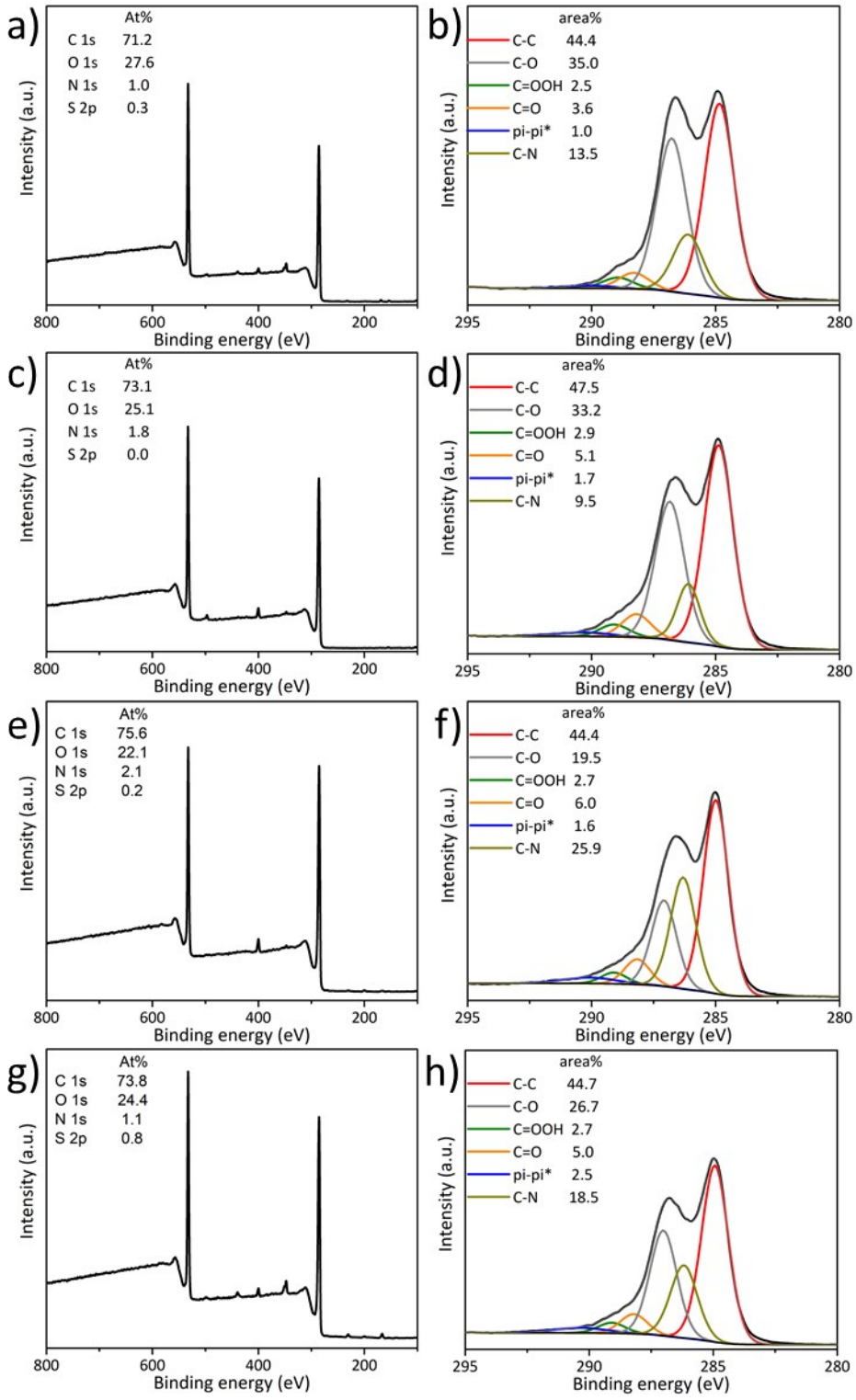


Figure S3. XPS survey spectra (a, c, e, g) and high resolution C 1s (b, d, f, h) spectra of GO **2** (a, b), GO **3** (c, d), GO **4** (e, f) and GO **4-CTR** (g, h).

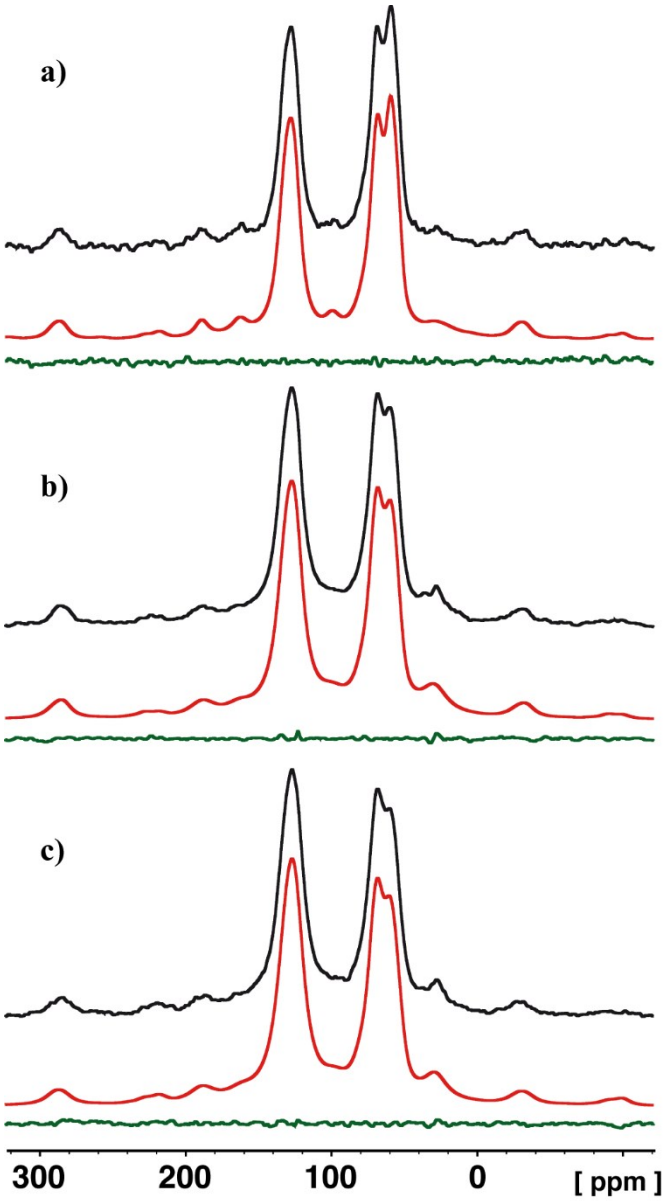


Figure S4. ^{13}C DP/MAS line shape analysis (experimental black, calculated red, difference green). a) pristine GO, b) GO **5a** and c) GO **5a-CTR**.

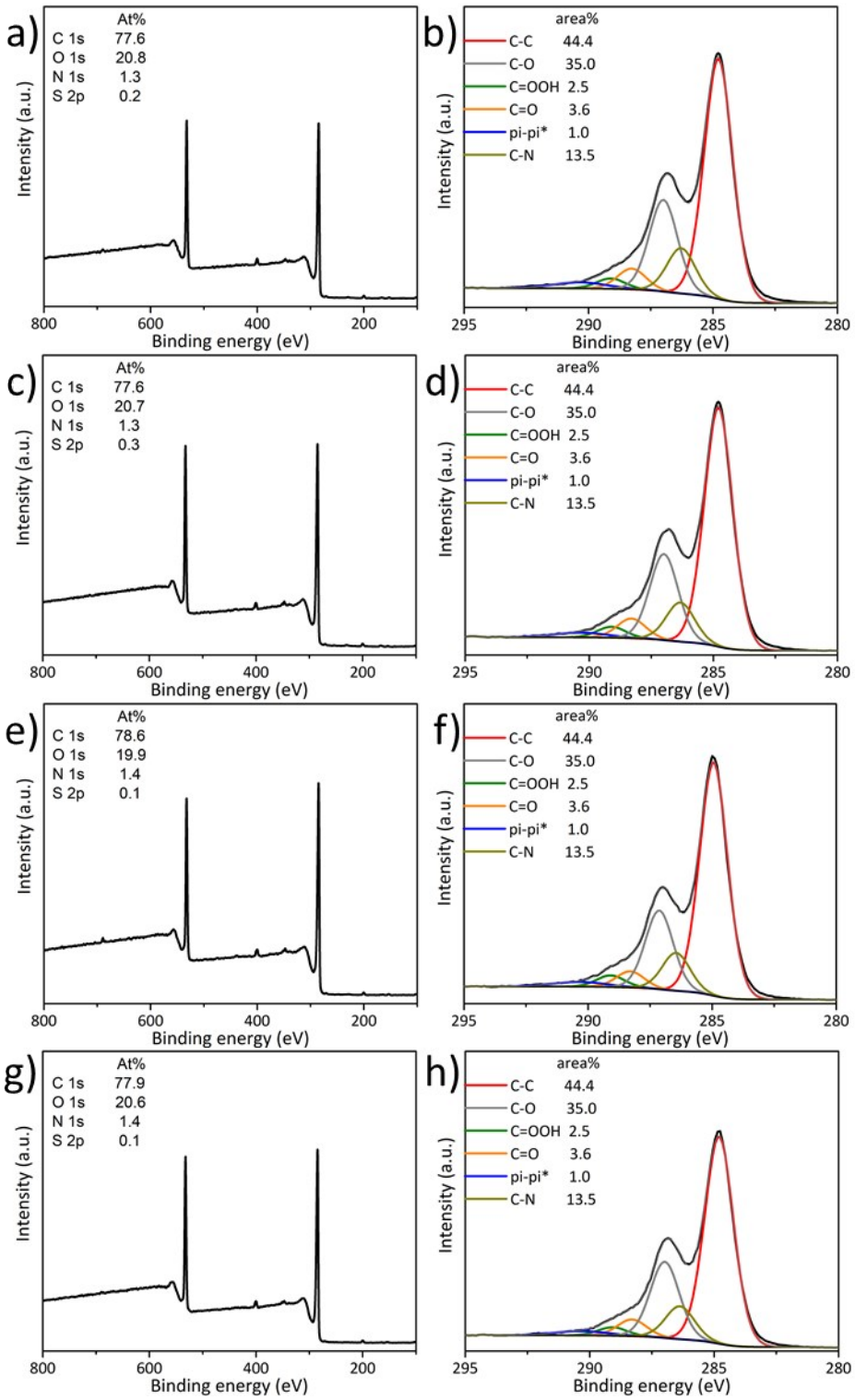


Figure S5. XPS survey spectra (a, c, e, g) and high resolution C 1s (b, d, f, h) spectra of GO **6a** (a, b), GO **6b** (c, d), GO **7a** (e, f) and GO **7b** (g, h).

Table S1. Percentages of the different peaks for pristine a) GO, b) GO **5a** and c) GO **5a-CTR** obtained from the quantitative ^{13}C NMR spectra.

a)

δ (ppm)	%
190.2	2
164.0	3
132.3	23
126.7	17
100.4	2
78.3	4
69.8	20
60.1	22
55.0	2
27.0	4

b)

δ (ppm)	%
189.7	3
164.5	2
131.8	25
125.9	18
100.4	3
80.8	2
70.2	23
60.4	16
55.9	2
30.6	6

c)

δ (ppm)	%
189.9	3
164.4	2
131.3	28
125.6	18
99.0	3
81.1	2
70.3	22
60.3	16
55.1	2
29.9	5

References

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