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Engineering of carbon based nanomaterials by ring-opening reaction of reactive azlactone graphene platform

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Electronic Supplementary Information

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Experimental Section

All reagents and solvents were obtained from commercial suppliers and used without further purification. Natural graphite powder (diameter 5–10 μm, thickness 4–20 nm, layers <30 and purity >99.5 wt%) was purchased from Sigma Aldrich. Melting points were determined on a Kofler melting apparatus and are uncorrected. Merck Kieselgel $60F_{254}$ plates were used for TLC and Merck silica gel 60 (0.063- 0.100 mm) for column chromatography. ^{1}H-NMR spectra were obtained with a Bruker AMX R300 and Varian 500MHz spectrometers. The chemical composition and the bonding configurations of the samples were investigated by means of X-ray Photoelectron Spectroscopy (XPS). The spectra were acquired at room temperature using a Thermo Scientific K-Alpha system, equipped with a monochromatic Al Kα source (1486.6 eV) and an hemispherical analyzer operating in constant-pass energy (CAE) mode. The pass-energy was set at 200 eV for survey scans and at 50 eV for the XPS core level spectra. A spot size diameter of about 400 μm was adopted while surface charging effects were avoided using an electron flood gun.

Raman spectra were carried out, in air at room temperature, using a Horiba XploRA spectrometer equipped with a confocal microscope and a Peltier-cooled charge-coupled detector (CCD). Spectra were excited using the 638 nm line from a solid state laser and integrated for 120 s, using a 50X long working distance microscope objective. In order to prevent laser induced damage or heating, measurements were carried out using a low laser power (2.5 mW on the illuminated area of 2.0 μm^2). Spectra from several random positions on each specimen were collected on account of the possible spatial non-homogeneity of the samples. The Fourier Transform Infrared (FTIR, Perkin Elmer Spectrum 100) spectra were collected, in Attenuated Total Reflectance (ATR) configuration, from 4000-450 cm^{-1}. The morphology of graphene samples was analyzed using an TEM, JEM2100 LaB6 operating at 200 kV, and a digital Scanning transmission electron microscopy (STEM) equipped with BF & DF STEM Detectors plus SE/BSE detector. TEM and STEM samples were prepared by placing five drops of the sample dispersed in isopropanol (≅0.5 mg/mL) on 300 mesh holey-carbon coated copper grids. Thermogravimetric analysis (TGA) was done by using a Perkin–Elmer TGA7 in the temperature range 50-800 °C. About 5 mg of each sample was, firstly, placed in an platinum pan and kept at 25 °C under a 60 ml/min N_2 flow until balance stabilization and subsequently heated with a scan rate of 10 °C/min under the same N_2 flux. Balance sensitivity was 0,1 µgr. A baseline recorded in the same measurement conditions with empty platinum pan was subtracted from each thermogram before data analysis. The MALDI-TOF mass spectra were collected by a Voyager DE (PerSeptive Biosystem) equipped with a nitrogen laser (emission at 337 nm for 3 ns) and a flash AD converter (time base 2 ns). In order to avoid fragmentation of the sample, the laser irradiance was maintained slightly above threshold. Each spectrum was an average of 32 laser shots. The MALDI-TOF investigations were performed by loading on the plate 0.4 mmol matrix trans-2-[3-(4-tert-butylphenyl)-2-methyl-2propenylidene]-malonitrile (DCTB) and 0.005 mmol of sample, using $CHCl_3$ or DMF as solvent. Both 5,10-di(p-dodecanoxyphenyl)-15,20-di(p-hydroxyphenyl) porphyrin ($C_{68}H_{78}N_4O_4$, 1014 Da), tetrakis(p-dodecanoxyphenyl)porphyrin ($C_{92}H_{126}N_4O_4$, 1350 Da) and a PEG sample of known structure were used as external standards for m/z calibration. The MALDI-TOF mass spectra were elaborated with Grams software (ver. 3.04), from Perseptive Biosystems.

SYNTHESIS OF AZIDOAZLACTON (4)

Synthesis of 4-(azidomethyl)benzoyl chloride (1)

A solution of 4-bromomethyl benzoic acid (2.23 g, 13 mmol) and sodium azide (2.55 g, 39,2 mmol) (*Use with Caution*!) in DMSO (10 mL) was stirred for 48h at 80 °C. After cooling to room temperature, 10 mL of deionized water and 20 mL of Et_2O were added. The organic phase was extracted with water and dried over $MgSO_4$; the solvent was removed under reduced pressure to obtain the pure 4-azomethyl benzoic acid [1] (2.1 g , yield 95%) . Thionyl chloride (1.2 mL,) was added to 4-azomethyl benzoic acid (540 mg, 95.66 mmol) at 0°C; the reaction was left at room temperature for 4 h under stirred and then at 50°C for 12 h. The reaction mixture was dried under reduced pressure to obtain an oil that was used without purification.

Synthesis of 2-(4-azidomethyl)benzamido)-2-methylpropanoic acid (3).

A solution of 4-(azidomethyl)benzoyl chloride **(1)** (497 mg, 2.55 mmol) in dioxane (5 mL) was added dropwise to mixture of 2-amino-2-methylpropanoic acid (263.9 mg, 2.55 mmol) and 756.8 mg of Na_2CO_3 in 10mL of deionized water. The solution was stirred overnight at room temperature. The solvent was removed under reduced pressure and the residue was treated with chloroform. The white precipitate was removed and the organic solvent was dried under reduced pressure to obtained 400 mg of **(3)**. No sign of product decomposition is evident until the dry powder was heated to 80 °C. *2-(4-azidomethyl)benzamido)-2-methylpropanoic acid* **(3)**: white solid, 58 % yield, mp 172-175°C: ^{1}H NMR (500 MHz, $CDCl_3$) 1.77 (s, 6H), 4.49(s, 2H), 6.74(bs, 1H, NH), 7.38(d, 2H, *J*=8.3

Hz), 7.79(d, 2H, *J*=8.3 Hz), 7.95(bs, 1H, OH). ^{13}C NMR (125 MHz) 24.5, 24.9, 54.2, 57.1, 127.3, 127.7, 128.0, 128.5, 133.9, 139.4, 167.0, 177.9. MALDI-TOF (m/z): 263.3 [MH^+] cld for $C_{12}H_{14}N_4O_3$ 262.1.

Synthesis of 2-(4-azidomethyl)phenyl)-4,4-dimethyloxazol-5(4*H*)one (4)

To a solution of **(3)** (145 mg, 0.55 mmol) in dry acetonitrile (1 mL), ethyl chloroformate (52 μL) was added under argon inlet. The reaction mixture was stirred for 30 min at room temperature; then the temperature was decreased at 5°C and triethylamine (152 μL) was added. The reaction was stirred for 2h at room temperature and for an additional hour at 40°C. The formed precipitate was removed by filtration and the supernatant dried to a yellow oil under reduced pressure. The residue was extracted using hot hexane, the solutions were collected and dried under reduced pressure to obtain 110 mg of **(4)**. No sign of product decomposition is evident until the dry powder was heated to 80 °C. *2-(4-azidomethyl)phenyl)-4,4-dimethyloxazol-5(4H)one* **(4)**, yellow oil, 76%, ^{1}H NMR (500 MHz, $CDCl_3$) 1.23(s, 6H), 4.41(s, 2H), 7.42(d, 2H, *J*= 6.3 Hz), 7.99(d, 2H, *J*= 6.3 Hz). ^{13}C NMR (125 MHz) 24.7, 24.8, 54.2, 65.9, 125.9, 128.2, 128.3, 128.4, 140.2, 159.0, 181.0. MALDI-TOF (m/z): 245.2 [MH^+] cld for $C_{12}H_{12}N_4O_2$ 244.1.

PREPARATION OF GRAPHENE BASE MATERIALS (GO and G-Red)

Graphene oxide (GO) was prepared by oxidizing natural graphite powders using Hummers method[2] and successive exfoliation of graphite oxide by ultrasonication. **GO** was reduced with hydrazine, under controlled conditions, according to literature[3] procedure to obtain reduced graphene sheets (**G-Red**) (Fig.S1)

Fig.S1 Schematic illustration of the preparation of reduced graphene (**G-red**)

Briefly, natural graphite (2 g) was added to sulfuric acid (350 mL) cooled at 0°C and the mixture was vigorously stirred to avoid agglomeration. When the graphite was well dispersed, sodium nitrate (1g) and potassium permanganate (8 g) were, very slowly and contemporaneously, added to the reaction mixture. The temperature was then raised up to 40°C and the mixture was stirred for 1 h. Thereafter, deionized water (250 mL) was slowly added into the solution, determining an immediate increase of temperature up to 70°C. The temperature was raised up to 98°C and the reaction stirred for 30 min. Finally, 52 mL of H_2O_2 30% were poured into the reaction mixture, resulting in the formation of bright yellow suspension. The graphite oxide was separated by vacuum filtration and washed with diluted HCl (4%) and water to reach a neutral pH. The product was dried to obtain a brown powder (1.8 g). Exfoliation of graphite oxide was carried out by ultrasonication (40% W, 8h) of the aqueous suspension graphite oxide (500 mg of graphite oxide in 35 mL of deionized water). The obtained homogeneous dark brown dispersion was diluted with deionized water and ultracentrifugated at 10000 rpm for 12 min; then, the residue was eliminated and the supernatant contains the graphene oxide sheets (GO) were recovered. GO powders were obtained by freeze-drying of supernatant (300 mg). From TGA analysis under N_2 atmosphere weight loss of 51% , due the decomposition of the surface groups heated up to 600 °C, was estimated. The reduced graphite oxide (**G-red**) was obtained by reduction of the GO with hydrazine, according to literature procedure.[2] The GO powders (100 mg) were dispersed in deionized water at concentration of 3 mg/1mL and sonicated for 3 h; 33μL of 98% Hydrazine was added and the reaction mixture was stirred at 80°C overnight. The reduced graphene (**G-red**) precipitate was filtered under vacuum on

Millipore membrane of 0.1 μm and washed with deionized water. The residue was dried under vacuum at 50 °C to give 70 mg of **G-red**. From TGA analysis under N_2 atmosphere a weight loss of 15 % due the decomposition of the surface groups heated up to 600 °C was estimated.

Characterization of graphene based materials

The graphene base materials graphene oxide (**GO**) and reduced graphene (**G-red**) have been characterized by TGA (Fig. S2) , XPS (Fig S8) Raman (Fig S6) and TEM (Fig. S10) analyses. The results are in agreement with literature data.[2,3]

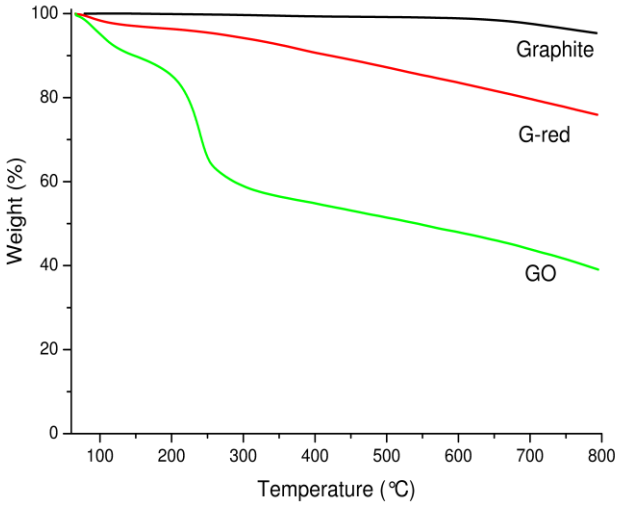

Fig.S2 TGA profiles of **Grafite**, **GO** and **G-red**, under N_2 atmosphere.

PREPARATION OF REACTIVE AZLACTONE GRAPHENE PLATFORM (RAGP)

Preparation of alkyne-terminated graphene (G-Alk)

The aryldiazonium ion solution was prepared following the method described below.

Sodium nitrite (329 mg, 4.76 mmol) was slowly added, at 0 °C under stirring, to a solution of p-(2-propylnyloxy)-benzammine (**5**) (638 mg, 4.34 mmol) in HCl 37% (82.21 mL). Then, 2.17 mL of HCl 20% were dropwise added and the reaction was stirred at 0°C for 45 min.

G-red, (171 mg) dispersed in deionized water (100 mL) was sonicated at room temperature for 1 h to obtain a homogeneous black suspension. The diazonium salt solution was added to the black suspension and the reaction mixture was sonicated at 0°C for 6 h. The reaction mixture was diluted with deionized water and centrifuged at 6000 rpm for 20 min. The precipitate was repeatedly washed with a solution of deionized water and methanol (1:1), the supernatant was discharged after centrifugation at 6000 rpm for 20 min and the residue was dried at 60°C to give 56 mg of **G-Alk**. From TGA analysis, under N_2 atmosphere, the amount of alkyne moiety grafted on the graphene surface was estimated to be ~11 wt % corresponding to~0.8 mmol /g.

Dispersion stability

The treatment of reduced graphene with diazonium compounds improve the dispersibility in water and prevent the aggregation of graphene sheets. **Fig.S3** shows photographs of **G-red** and **G-Alk** dispersed in distilled water (2 mg/mL) three days after the preparation.

Fig.S3 Photographs of **G-red** and **G-Alk** dispersed in water (2 mg/mL) three days after preparation.

Preparation of reactive azlactone graphene platform (RAGP)

Alkyne-terminated graphene **(G-Alk)** (20 mg) in 10 mL of dry DMF were sonicated at room temperature for 30 min to obtain a homogeneous black suspension. Azido-azlactone (**4**) (20 mg, 0.081 mmol), sodium ascorbate (8.5 mg, 0.043 mmol) and copper sulfate (3.65 mg, 0.022 mmol) were added at room temperature under argon inlet. Then the temperature was increased up to 80°C and the reaction was stirred at 80°C for 48 h under argon inlet. The reaction mixture was diluted with deionized water and centrifuged at 6000 rpm for 20 min. The supernatant was discharged and the residue was repeatedly washed with a solution of deionized water/methanol (1:1) and again centrifuged at 6000 rpm for 20 min. The precipitate was dried at 60°C to give 23 mg of **RAGP**. From TGA analysis under N_2 atmosphere the amount of linked oxazolone moiety was estimated to be ~8.3 wt % corresponding to~0.3 mmol /g.

RING OPENING REACTIONS

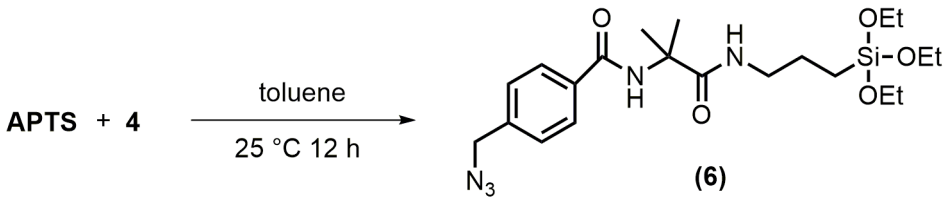

Fig. S4 Ring opening reactions of **(4)** with **APTS**

Reaction of **(4)** *with aminopropyltriethoxysilane (APTS)*

0.028 mL of APTS (0.122 mmol) were added to a solution of azlactone **(4)** (30 mg, 0.122 mmol), in toluene (2 mL). The reaction was allowed to stir at room temperature overnight. The solvent was removed under reduced pressure to obtain (**6)** (58 mg).

N-(2-(3-(triethoxysilyl)propylcarbamoyl)propan-2-yl)-4-(azidomethyl)benzamide **(6)**, white solid, 100% yield, mp 160-162 °C. ^{1}H NMR (300 MHz, $CDCl_3$) 0.62(t, 2H, *J*=9.0 Hz), 1.19(t, 9H, *J*= 9.1Hz), 1.62(q, 2H, *J*=9.0 Hz), 1.67 (s, 6H), 3.31(m, 2H), 3.80(q, 6H, *J*=9.1 Hz) 6.58(bs, 1H, N*H*),7.30(bs, 1H, N*H*), 7.38(d, 2H, *J*= 6.1 Hz), 7.81(d, 2H, *J*= 6.1 Hz); ^{13}C NMR (125 MHz) 7.5, 18.3, 22.7, 25.0, 42.1, 54.2, 54.4, 58.4, 58.5, 127.5, 128.2, 134.8, 138.8, 166.1, 174.6. MALDI-TOF (m/z): 488.3 [MNa^+] cld for $C_{21}H_{35}N_5O_5Si$ 465.2.

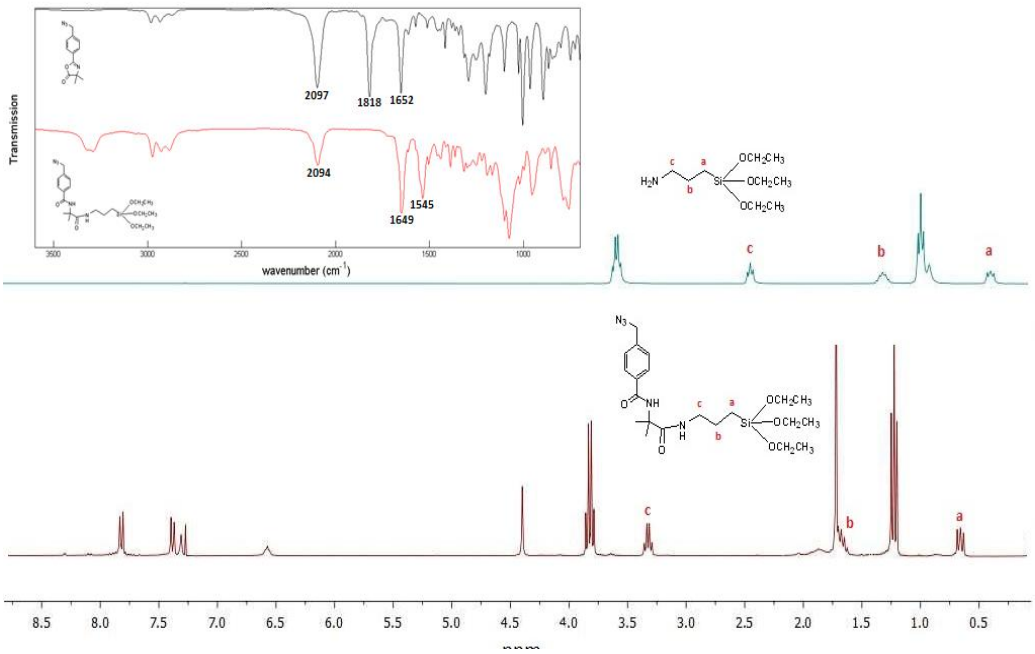

Fig. S5 ^{1}H NMR of APTS and crude reaction of **(6).** The inset shows the IR spectrum of **(4)** and crude reaction of **(6).**

Reaction of **RAGP** *with aminopropyltriethoxysilane (APTS)*

RAGP (25 mg) in 5 mL of DMF was sonicated at room temperature for 10 min to obtain a homogeneous black suspension. APTS (20 µL, 0.04 mmol) was added and the reaction mixture was stirred at room temperature overnight. The reaction mixture was diluted with deionized water and centrifuged at 10000 rpm for 10 min and the supernatant was discharged. The precipitate was repeatedly washed with a solution of deionized water and methanol (1:1), centrifuged at 10000 rpm for 15 min and the supernatants were discharged. The residue was dried at 60°C to give 20 mg of **GF-APTS**. From TGA analysis, under N_2 atmosphere, the amount of linked APTS was estimated to be ~22,8 wt % corresponding to~ 1.0 mmol /g

Reaction of **RAGP** *with oxidized glutathione (GSSG)*

GSSG (12.5 mg, 0.02 mmol) was added to a homogeneous black suspension of **RAGP** (25 mg) in DMF (5 mL) and the reaction was stirred at room temperature for 72 h. The reaction mixture was diluted with deionized water and centrifugated at 10000 rpm for 10 min. The precipitate was repeatedly washed with a solution of deionized water and methanol (1:1), centrifugated at 10000 rpm for 15 min and the supernatants were discharged. The residue was dried at 60°C to give 24 mg of **GF-GSSG.** From TGA analysis, under N_2 atmosphere, the amount of linked GSSG was estimated to be ~ 22.7 wt corresponding to~0.3 mmol /g

RAMAN ANALYSIS

Raman spectroscopy was used to probe structural characteristics of the investigated carbon-based materials providing useful information on the defects (D-band) related to the vibrations of the sp^3 hybridized carbons and located at about 1330 cm^{-1}, and in-plan vibration of sp^2 carbon atoms (G-band) centred at about 1580 cm^{-1}. Raman spectra are also characterized by the second-order Raman 2D band (known as D'), which is a defect-independent contribution. The effect of reduction process of Raman spectral profiles implies increased defect density, which explains the progressive decrease of the graphitization degree (i.e., of I_G/I_D in Fig. S6), confirming the highly disordered structure of the carbon.

Since functionalisation brings about an increase of the structural disorder in the graphitic lattice (e.g. the sp^2-defect), the I_G/I_D ratio decreases from 1.08 in the G-Alk sample down to 0.61 in the GF-APTS one. In the GF-APTS and GF-GSSG samples, the D- and G-bands bands slightly shift toward higher wavenumbers (from 1312 cm^{-1} and 1580 cm^{-1} in RAPG sample up to 1332-1341 cm^{-1} and 1588-1608 cm^{-1} in the GF-APTS and GF-GSSG ones, respectively) as an effect of the electron transfer from graphic lattice to oxygenated moieties (see Fig. S5), as confirmed by FTIR and XPS analyses. Thus, the typology of oxygenated functionalities have a significant impact on the wavenumber position of D and G bands. The addition of APTS and GSSG reflect also on the width (FWHM) of the Raman bands. FWHM slightly decreases, hinting a shrinkage of the distributions of the angles and lengths of C bonds as well as of the strains.

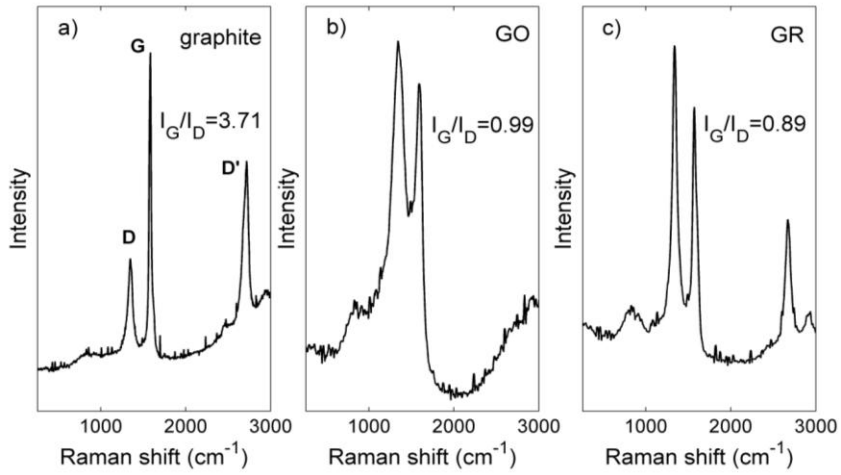

Fig. S6 Raman spectra of (a) graphite; (b) graphene oxide (**GO**); (c) reduced graphene oxide(**G-Red**)

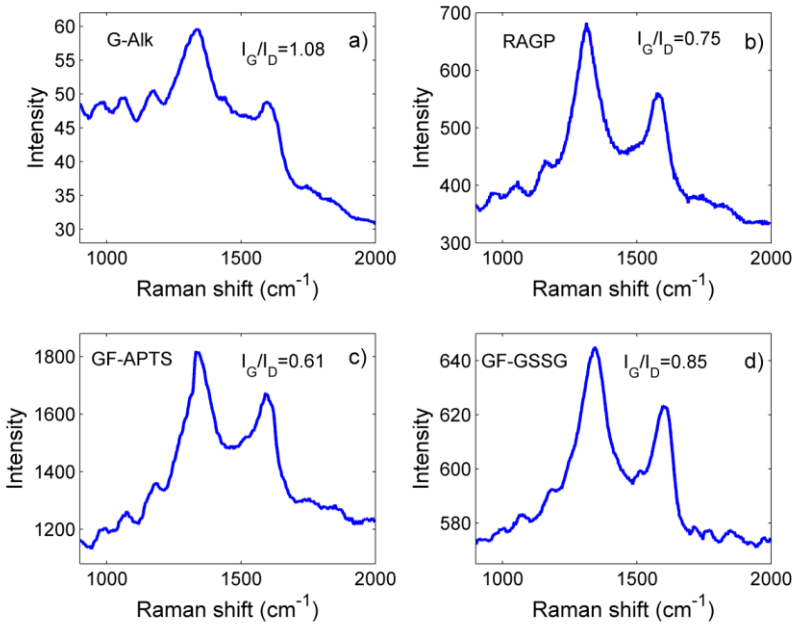

Fig. S7: Raman spectra of (a) G-Alk, (b) RAGP, (c) GF-APTS and (d) GF-GSSG samples

XPS ANALYSIS

High resolution XPS spectra of graphite, (GO) and (G-red)

For the deconvolution of the XPS spectra, a mixed Gaussian−Lorentzian sum function with inelastic Shirley-type background was used. The C 1s regions are composed of six contributions at about 284.5, 285.8, 286.6, 287.7, 288.9 eV and 291 eV. These contributions are ascribed to C=C/C-C in aromatic ring, C-OH, C-O-C, C=O and OH-C=O and π-π bounds, respectively. Then, the so-determined photoemission peak areas were converted into atomic concentrations using Scofield sensitivity factors.[4]

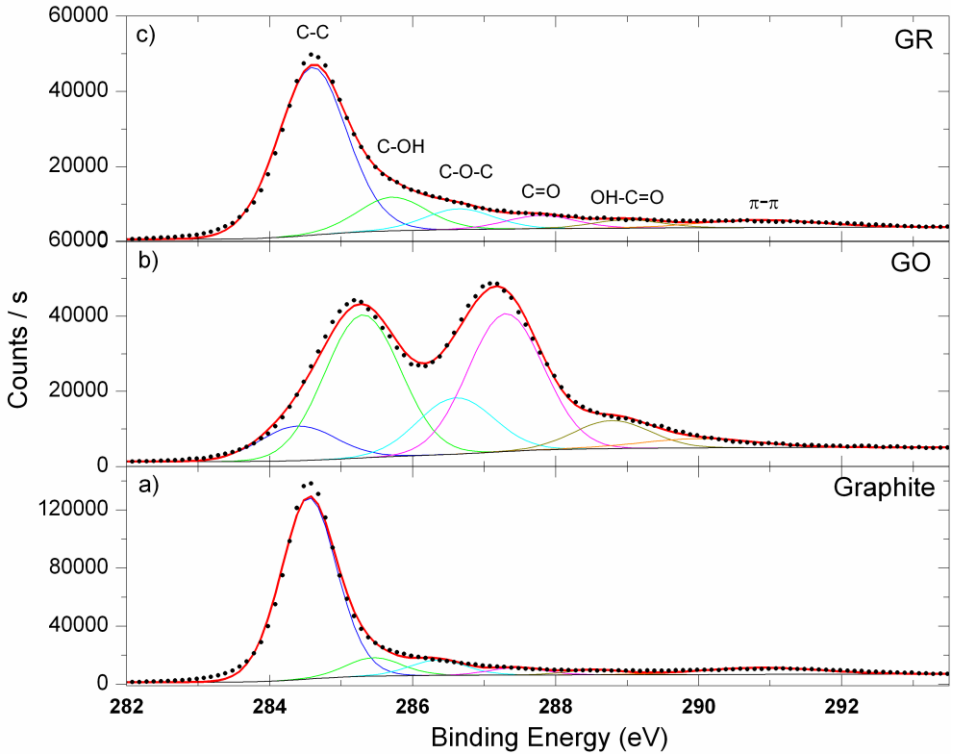

Fig. S8: C 1s X-ray photoelectron spectra of (a) graphite; (b) graphene oxide (**GO**); (c) reduced graphene oxide.(**G-red**)

Table S1: Relative percentage of functional groups obtained by fitting the C 1s XPS spectra.

Samples	C-C (%)	C-OH (%)	C-O-C (%)	C=O (%)	OH-C=O (%)	π-π(%)
Graphite	74,9	7,6	6,4	3,0	2,0	6,10
GO	8,3	34,5	13,6	33,3	6,8	3,5
G-red	65,3	13,1	8,1	5,1	3,3	5,1

Table S2: Atomic content percentage by XPS analysis

Samples	Si (%)	S (%)	Cl (%)	C (%)	N (%)	O (%)	Sn (%)	F1s (%)	Cu2p (%)
G-Alk	0,6	-----	0,3	83,9	3,7	11,1	0,1	0,3	-----
RAGP	0,4	-----	0,2	79,3	6,0	13,0	0,1	0,6	0,4
GF-APTS	21,5	-----	0,2	56,6	0,9	20,1	-----	0,7	-----
GF-GSSG	1,0	0,3	0,4	80,9	3,6	12,8	0,3	0,3	0,4

Table S3: Bonding fraction percentage by XPS data.

Samples	C-C (%)	C-OH (%)	C-O-C (%)	C=O(%)	O-C=O(%)	π-π(%)
G-Alk	64,2	15,7	8,3	4,8	3,2	3,8
RAGP	60,0	12,7	12,8	6,9	4,3	3,3
GF-APTS	87,2	5,0	4,2	1,8	1,3	0,5
GF-GSSG	63,7	16,2	7,9	5,0	4,4	2,8

Fourier transform infrared spectroscopy (FT-IR) Analysis

The presence of functional groups on the graphene surface is confirmed by FTIR spectra. In Fig.S7 are shown selected region of RAPG, GF-APTS and GF-GSSG IR spectra. The C=C stretching band at 1590 cm^{-1} of graphene is present in all the samples. The signal of C=O amide group at about 1630 cm^{-1} is indicative of the coupling of amine groups with azlactone moiety. Both in GF-APTS and GF-GSSG spectra are present the strong bands at approximately 2800 and 2900 cm^{-1} corresponding to sp^3 C-H stretching.

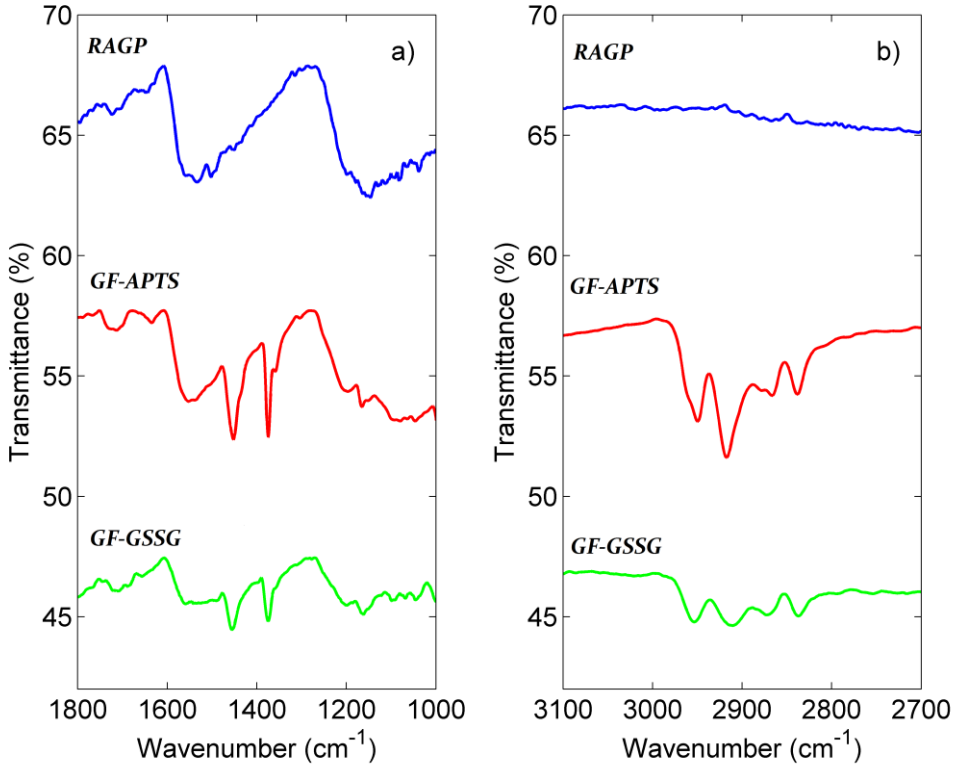

Fig. S9 FT-IR spectra of RAGP, GF-APTS and GF-GSSG samples.

TEM AND STEM ANALYSIS

TEM micrograph of GO showed that GO is partially folded due to large area occupied; the images of G-red and G-Alk showed sheets homogeneous and quite smooth, with little aggregation (Fig S10 ESI).

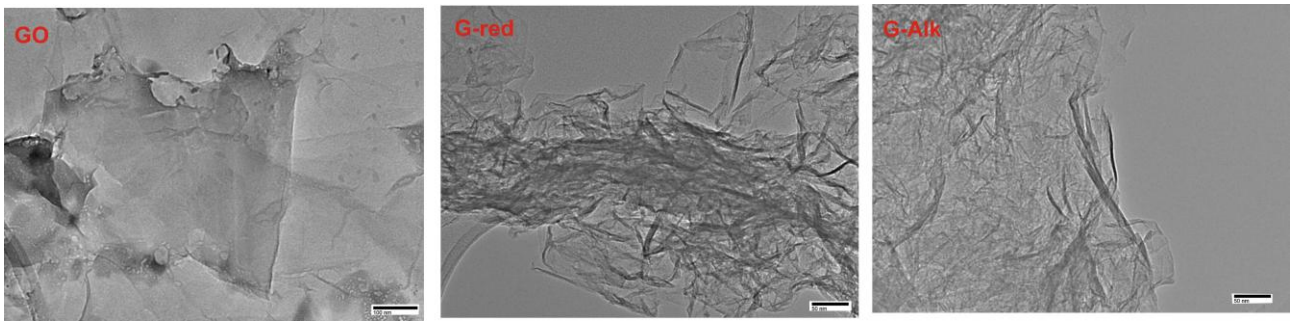

Fig. S10 TEM images of graphene based materials: **GO**, **G-red**, **G-Alk**.

Fig. S11-S13 show STEM images with linescan percentage elemental analysis for C, N and O in RAGP (Fig.S11), C,N, O and Si in GF-APTS (Fig. S12) and C, N, O, and S in GF-GSSG (Fig. S13). Three elements as carbon, oxygen and nitrogen are dispersed in the samples, and the content of these three elements is similar in RAGP and APTS, respectively whereas is reduced in GF-

GSSG. The lower amount of peculiar elements as S in GF-GSSG with respect to Si in GF- APTS suggests an additional grafting of APTS on the graphene surfaces; probably, on residual phenolic and carbonyl groups.[5]

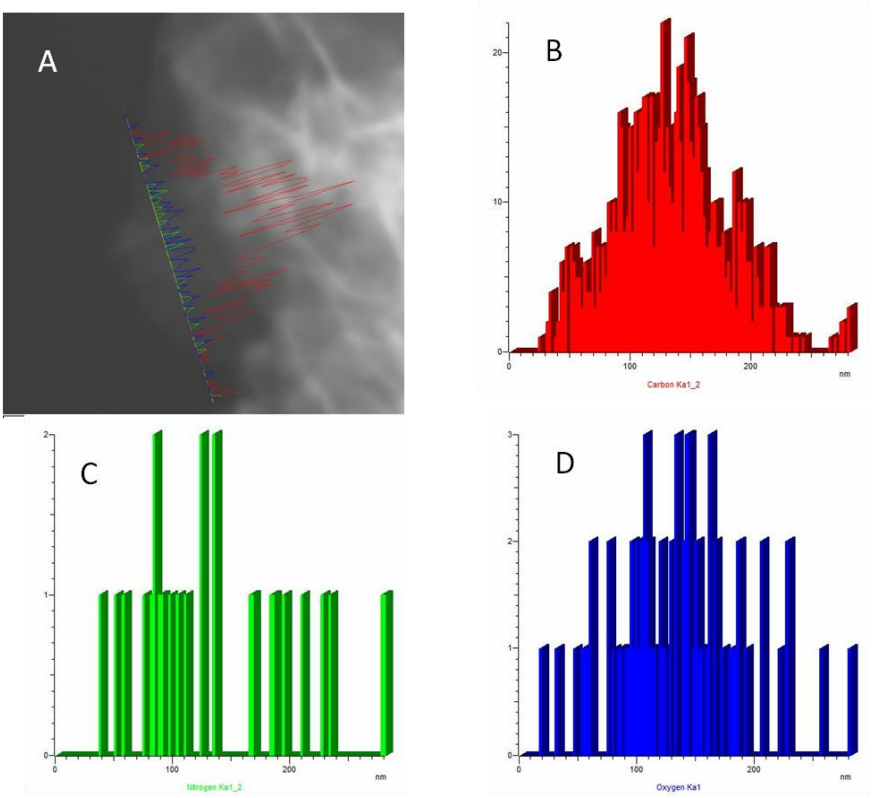

Fig. S11 a) STEM of RAGP with linescans and total element percentage, detected by peculiar emission lines; b) % of C c) % of N; d) % of O: distribution maxima at fixed scale-lenght (~ 120 nm): ~ 22% (C), 2% (N), 3% (O).

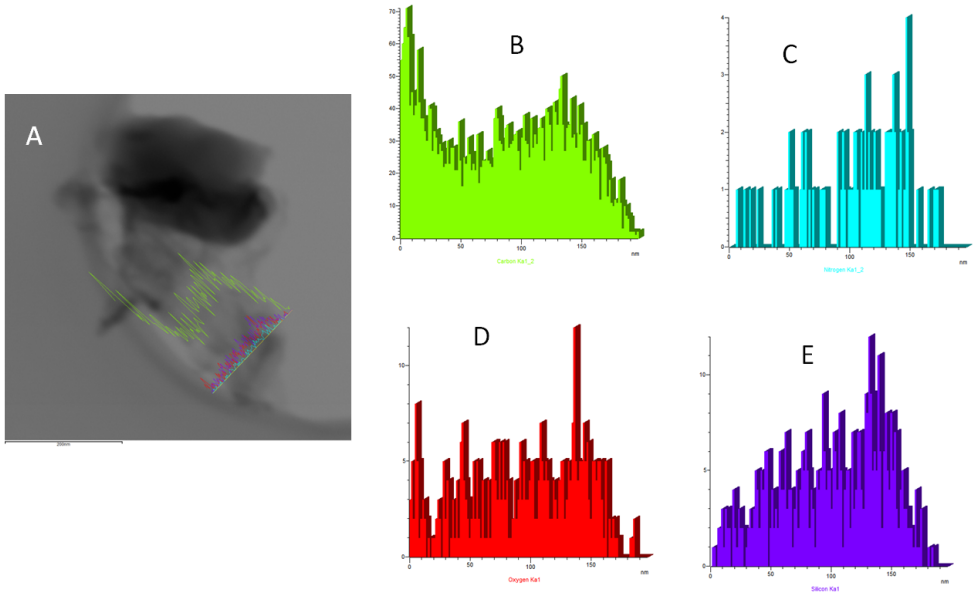

Fig. S12 a): STEM of GF-APTS with linescans and total element percentage, detected by peculiar emission lines; b) % of C; c) % of N; d) % of O; e) % of Si: distribution maxima at fixed scale-lenght (~140 nm): ~50% (C), 4% (N), 12% (O), 12% (Si).

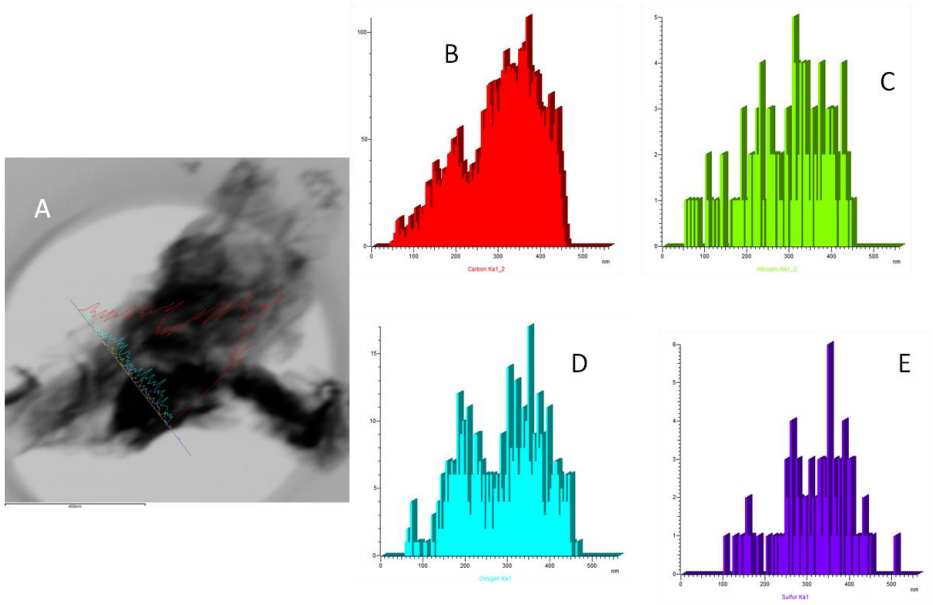

Fig.S13 a) STEM of GF-GSSG with linescans and total element percentage, detected by peculiar emission lines; b) % of C; c) % of N; d) % of O; e) % of S: distribution maxima at fixed scale-lenght (~ 350 nm): ~ 100% (C), 4.5% (N), 17% (O), 6%(S)

Proposed structure of GF-APTS

Based on our experimental results and according to literature data[5] we proposed the structure reported in Fig S14 for GF-APTS. We suggest that additional reactions between the silyl group of APTS and the phenolic and carboxylic groups occurred when RAGP was treated with APTS. In the case of functionalization with GSSG the residue carboxylic groups cannot react with amino groups of GSSG without a coupling reagent.

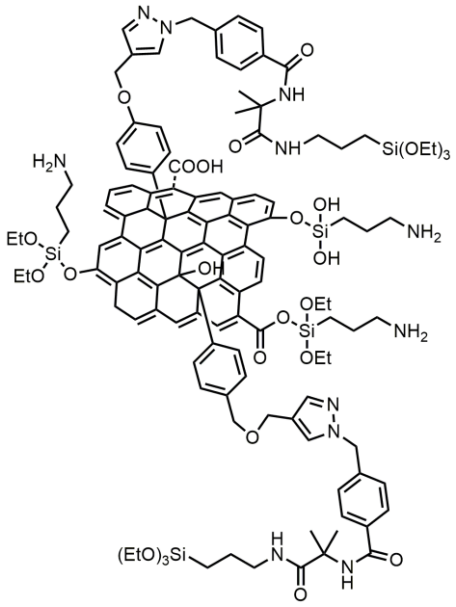

Fig.S14 Proposed structure of GF-APTS

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