Electronic Supporting Information

Modulating Charge Carrier Density and Mobility in Doped Graphene by Covalent Functionalization

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Materials and Instrumentation

Nitrogen-doped graphene [N(G), grade TNNRGO] with a nitrogen content of 5~10% wt was supplied by Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences (Chengdu, China) (www.timesnano.com). Boron-doped graphene (B(G)) was synthesized according to literature procedure.[1]

Organic solvents and reagents used in this work were purchased from commercial suppliers and used as received, unless otherwise stated.

Sample sonication was carried out using an Elmasonic P 300 h sonicator bath (37 kHz).

FTIR spectra were recorded on a Fourier Transform IR spectrophotometer (Avatar 370) in the range of 4000-400 cm^{-1}, with a resolution of 1 cm^{-1}, and in pellets of dispersed samples of the corresponding materials in dried KBr.

Thermogravimetric analyses (TGA) were performed using a TGA/DSC Linea Excellent instrument by Mettler-Toledo, collected under a flow of nitrogen (90 $mL.min^{-1}$). The sample (~ 0.5 mg) was introduced into a platinum crucible and equilibrated at 40 ºC followed by a 10 °C/min ramp between 40 ºC and 1000 °C. The weight changes were recorded as a function of temperature.

X-ray photoelectron spectra (XPS): XPSK-ALPHA, Thermo Scientific was used to analyse the samples surface. All spectra were collected using Al-K radiation (1486.6 eV), monochromatized by a twin crystal monochromator, to yield a focused X-ray spot (elliptical in shape with a major axis length of 400 µm) at 3 mA × 12 kV. The alpha hemispherical analyser was operated in the constant energy mode with survey scan pass energies of 200 eV to measure the whole energy band and 50 eV in a narrow scan to measure specific elements selectivity. XPS data were analysed with Avantage software. A smart background function was used to approximate the experimental backgrounds and surface elemental composition were calculated from background-subtracted peak areas. Charge compensation was achieved with the flood gun system, which provides low energy electrons and low energy argon ions from a single source.

Raman spectra were obtained on a Renishaw inVia Raman instrument coupled with a Leica microscope at room temperature with a 532 nm exciting laser. The samples were deposited on SiO_2 wafers.

AFM images were acquired in tapping mode using a Multimode V8.10 system (Veeco Instruments Inc., Santa Barbara, USA) with a NanoScope V controller (Digital Instruments, Santa Barbara, USA) operating at room temperature in ambient air conditions. The cantilevers (RTESP from Bruke Probes) were silicon cantilevers with a resonance frequency of 300 kHz and a nominal force constant of 40 $Nm.^{-1}$ The functionalized samples (0.2 mg m^{-1}) were prepared by sonication (frequency: 37 kHz; power 380 W) in ethanol for 1500 min, followed by ultracentrifugation at 13000 rpm for 5 min to remove the heavier material. Samples were prepared by spin coating on SiO_2 surfaces previously functionalized with (3-aminopropyl)triethoxysilane.

X-ray diffraction patterns were obtained in a Philips X'Pert diffractometer using the copper radiation (Cu–Kα = 1.54178 Å).

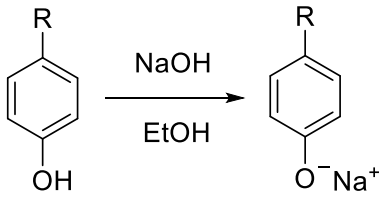
Exfoliation procedure

For **B(G)** material: B(G) (1 mg) was dispersed in distilled water (1 mL) at room temperature using an Elmasonic P 300 H sonicator bath (37 kHz). After 120 min of sonication, the resulting dispersion was centrifuged for 10 min at 500 rpm and the supernatant was separated from the product on the bottom of the vessel by pipetting the liquid phase.

For **N(G)** material: N(G) (1 mg) were dispersed in *N*-methyl 1-pyrrolidone (NMP) (3 mL) at room temperature using an Elmasonic P 300 H sonicator bath (37 kHz). After 30 min of sonication, the resulting dispersion was centrifuged for 10 min at 500 rpm and the supernatant was separated from the product on the bottom of the vessel by pipetting the liquid phase.

In both cases, the concentration in the resulting dispersions was determined by recording the absorbance at 660 nm and transforming this into the concentration using the Lambert-Beer law $A/l=\alpha c$ with a $\alpha=2.460$ $mLmg^{-1}$ $m.^{-1}$

Synthetic procedure for phenolates 5-6:[2]



5, R= OCH_3
6, R= NO_2

Sodium hydroxide (16.7 mmol, 1 eq) in anhydrous ethanol (5 mL) was added dropwise to a solution of the corresponding substituted phenol derivative (14.4 mmol, 1.1 eq) in ethanol (4 mL). The reaction solution was stirred at room temperature for 30 min. The precipitate was filtered off and washed with cold diethyl ether to remove the starting material. The solid residue was dried under vacuum to afford the corresponding sodium methoxyphenolate **5** and sodium nitrophenolathe **6** in yields of 82 % and 98 %, respectively.

5: ^{1}H NMR (400 MHz, [D_6] DMSO) δ/ppm: 6.52 (d, ^3J = 8.9 Hz, 2H), 6.36 (d, ^3J = 8.8 Hz, 2H), 3.57 (s, 3 H, CH_3).

6: ^{1}H NMR (400 MHz, [D_6] DMSO) δ/ppm: 7.75 (d, ^3J = 9.4 Hz, 2H), 5.99 (d, ^3J = 9.4 Hz, 2H).

General synthetic procedure of *f*-B (G) materials 1 and 2:

To a suspension of exfoliated B-doped graphene (40 mg) in water (60 mL) was added the corresponding sodium phenolate [(**5**: 2433 mg, 16.6 mmol) or (**6**: 2766 mg, 16.6 mmol)] and the suspension sonicated for 15 min. The reaction mixture was stirred at 70 ºC for 3 d. The mixture was allowed to cool down to room temperature, filtered through a PTFE membrane (Millipore, 0.1 μm pore) and the black solid was collected and washed consecutively with water, methanol and dichloromethane until the filtrate becomes colourless. The black solid was dried overnight in a vacuum oven at 55 ºC to obtain ***f*-B(G) 1** and **2.**

General synthetic procedure of *f*-N(G) materials 3 and 4:

Synthesis of *f*-N(G) 3-4a (low degree of functionalization): A suspension of exfoliated N(G) (15 mg) in NMP (50 mL) was reacted with **9** (1560 mg, 6.2 mmol) or **10** (1460 g, 6.2 mmol) and K_2CO_3 as base (345 mg, 2.5 mmol). The reaction mixture was stirred at 120 ºC for 24 h. After cooling to room temperature, the suspension was filtered through a PTFE membrane (Millipore, 0.1µm pore) and the black solid was collected and washed consecutively with water, methanol and dichloromethane, until the filtrate become colourless. Black solid was dried overnight in a vacuum oven at 55 ºC to obtain ***f*-N (G) 3a** and **4a.**

Synthesis of *f*-N(G) 3-4b (high degree of functionalization): A suspension of exfoliated N(G) (25 mg) in NMP (50 mL) was reacted with **1** (500 mg, 2 mmol) or **2** (500 mg, 2.1 mmol), $CsCO_3$ (416.27 mg, 3.0 mmol) and CuBr (58 mg, 0.4 mmol). The reaction mixture was stirred at 150 ºC for 4 d. After cooling to room temperature, the suspension was filtered through a PTFE membrane (Millipore, 0.1µm pore) and the black solid was collected and washed repeatedly with water, methanol and dichloromethane, until the filtrate become colourless. ThebBlack solid was dried overnight in a vacuum oven at 55 ºC to obtain ***f*-N(G) 3b** and **4b**.

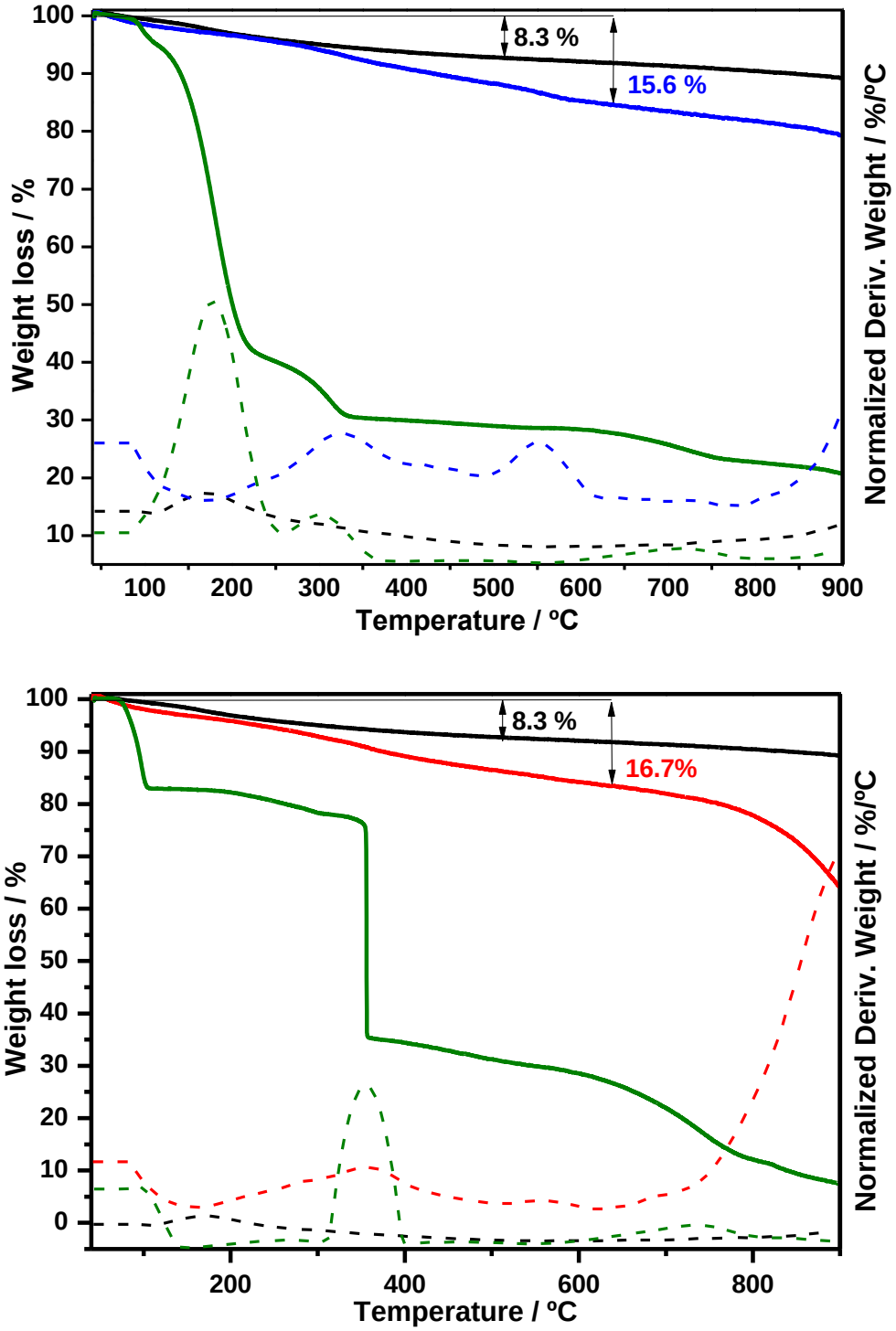


Figure S1. TGA profiles under inert conditions with first derivative of (upper panel) B(G) (—) and ***f*-B(G) 1** (—) and (bottom panel) **B(G)** (—) and ***f*-B(G) 2** (—), compared with sodium phenolate precursors (—).

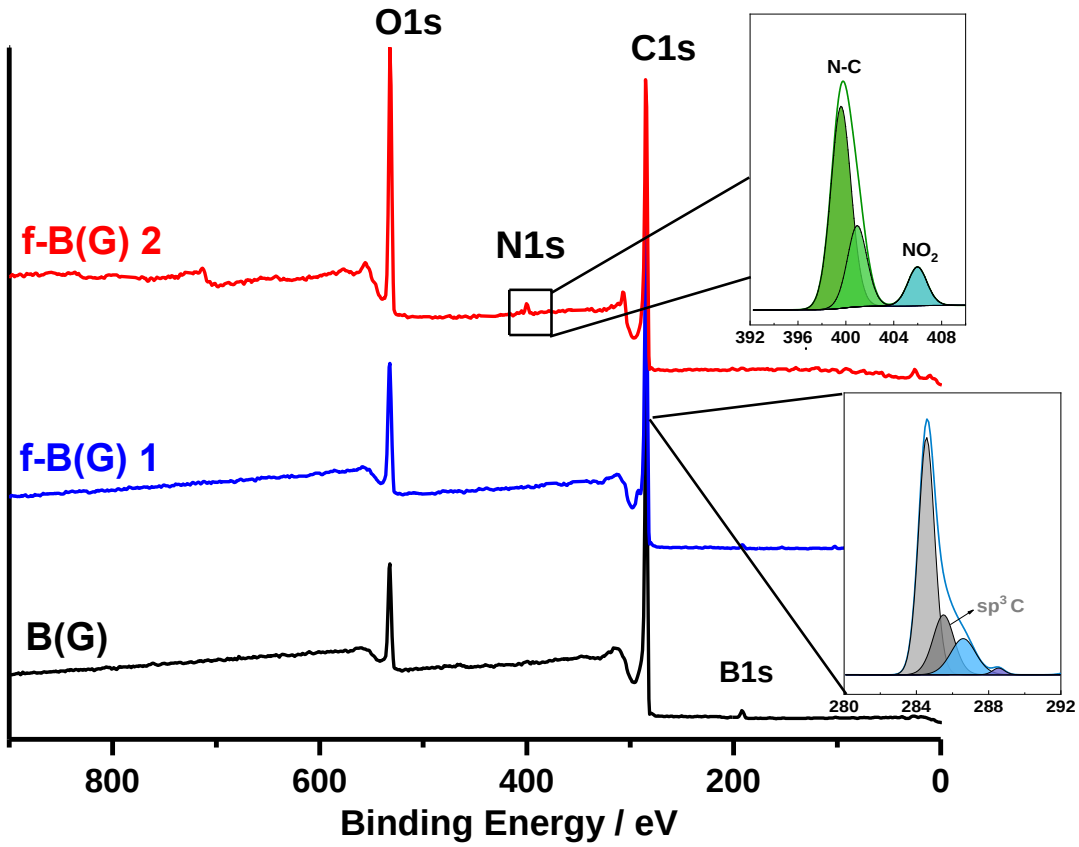


Fig. S2 XPS spectra of B(G) (—), ***f*-B(G) 1** (—) and ***f*-B(G) 2** (—). The insets correspond to the high-resolution C1s and the N1s peaks of ***f*-B(G) 1** and ***f*-B(G) 2**, respectively.

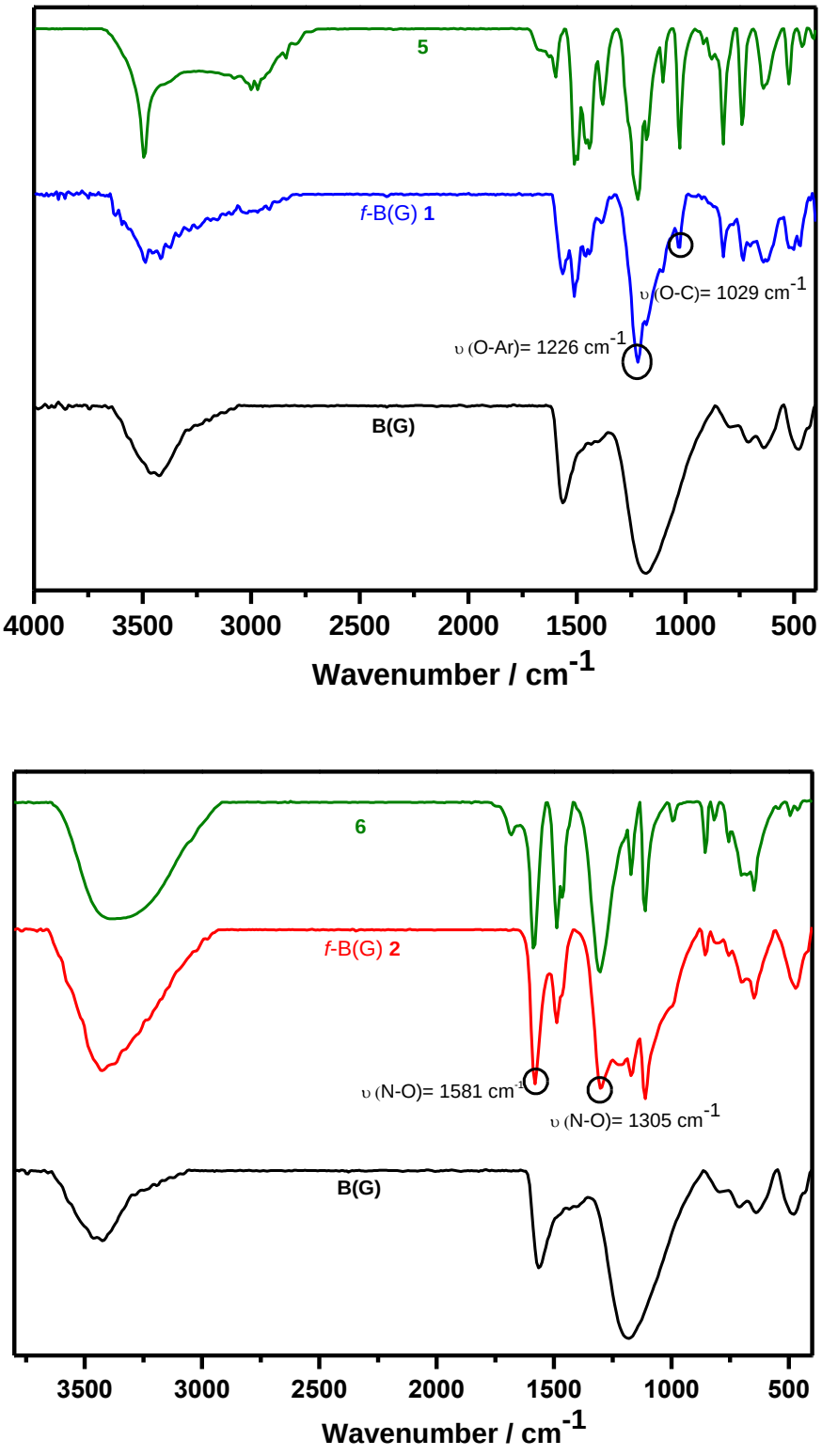


Figure S3. FT-IR spectra of (upper panel) B(G) compared to final hybrid ***f*-B(G) 1** and the corresponding phenolate **5** and (bottom panel) **B(G)** compared to final hybrid ***f*-B(G) 2** and the corresponding phenolate **6**.

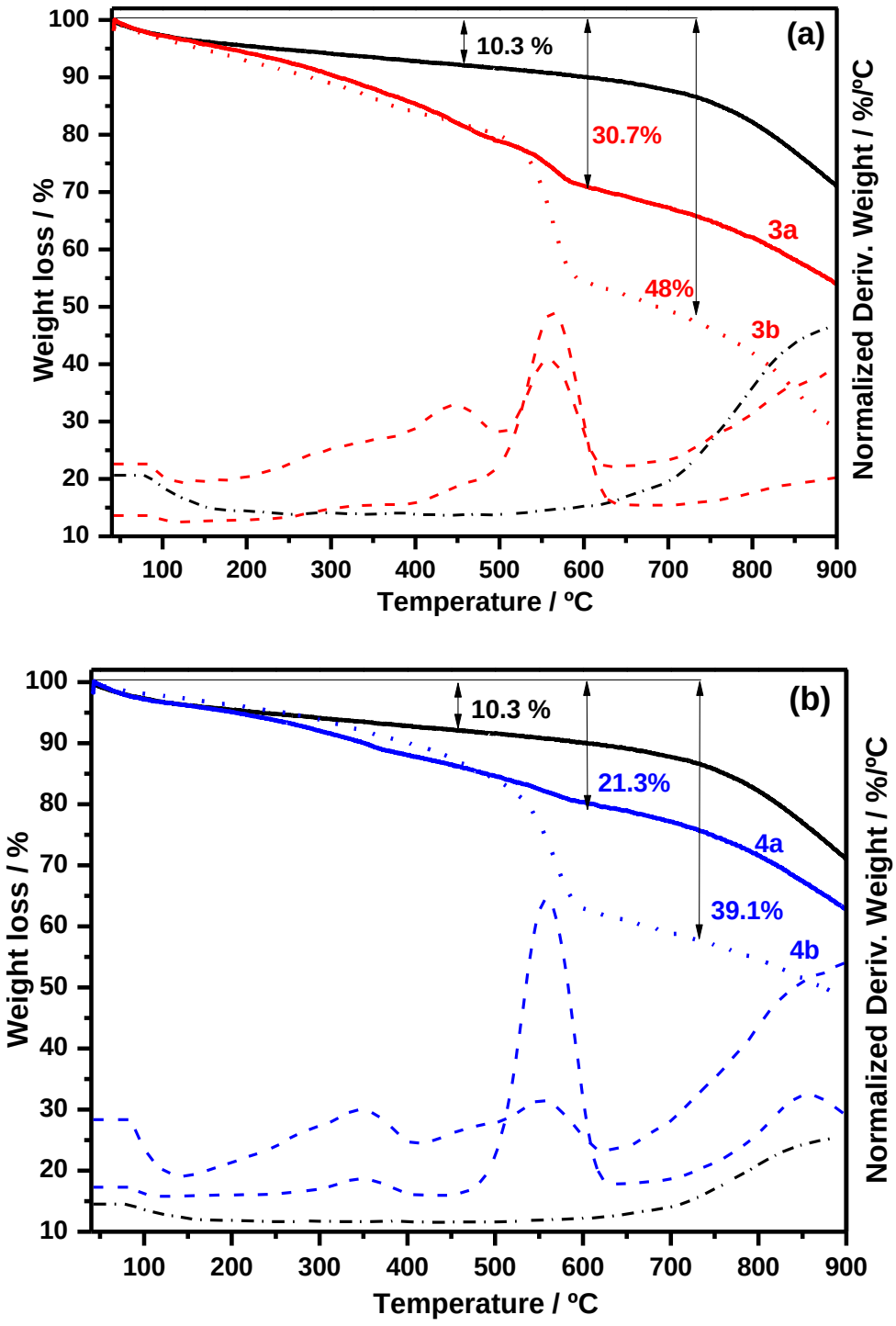


Figure S4. TGA profiles under a nitrogen atmosphere of (a) N(G) (—) and ***f*-N(G) 3a-b** materials (—) and (b) **N(G)** (—) and ***f*-N(G) 4a-b** (—). Note that dotted lines correspond to more functionalized materials.

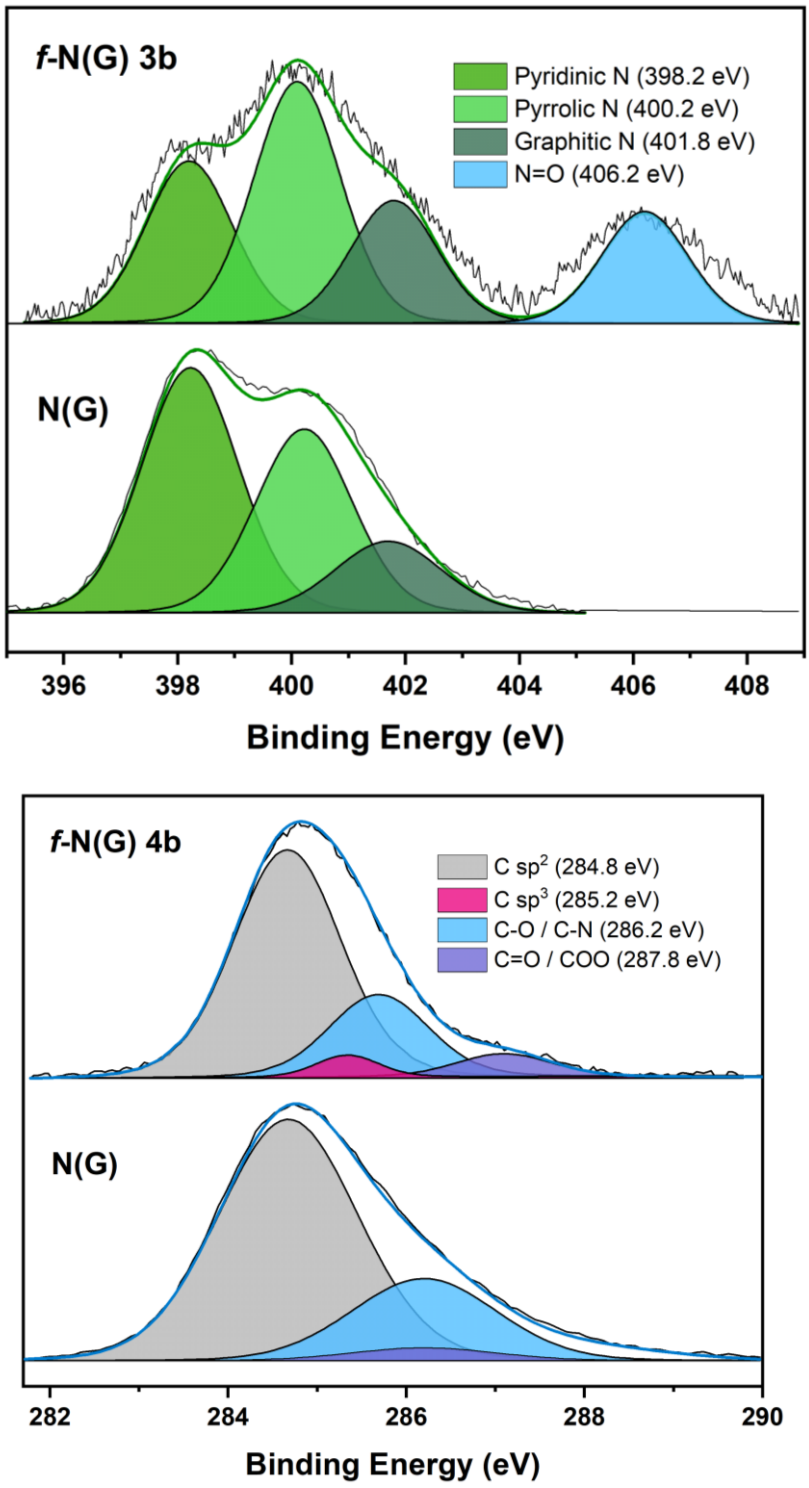


Fig. S5 (upper panel) XPS N1s core level spectra of N(G) compared to that of ***f*-N(G) 3b** and their relative fits, showing the nitro component at 406.2 eV (blue curve); (bottom panel) XPS C1s core level spectra of N(G) compared to that ***f*-N(G) 4b** and their relative fits, showing the sp^3 C component at 285.2 eV (magenta curve). The atomic percentages (at.%) of each component are shown in Table S4 in ESI.

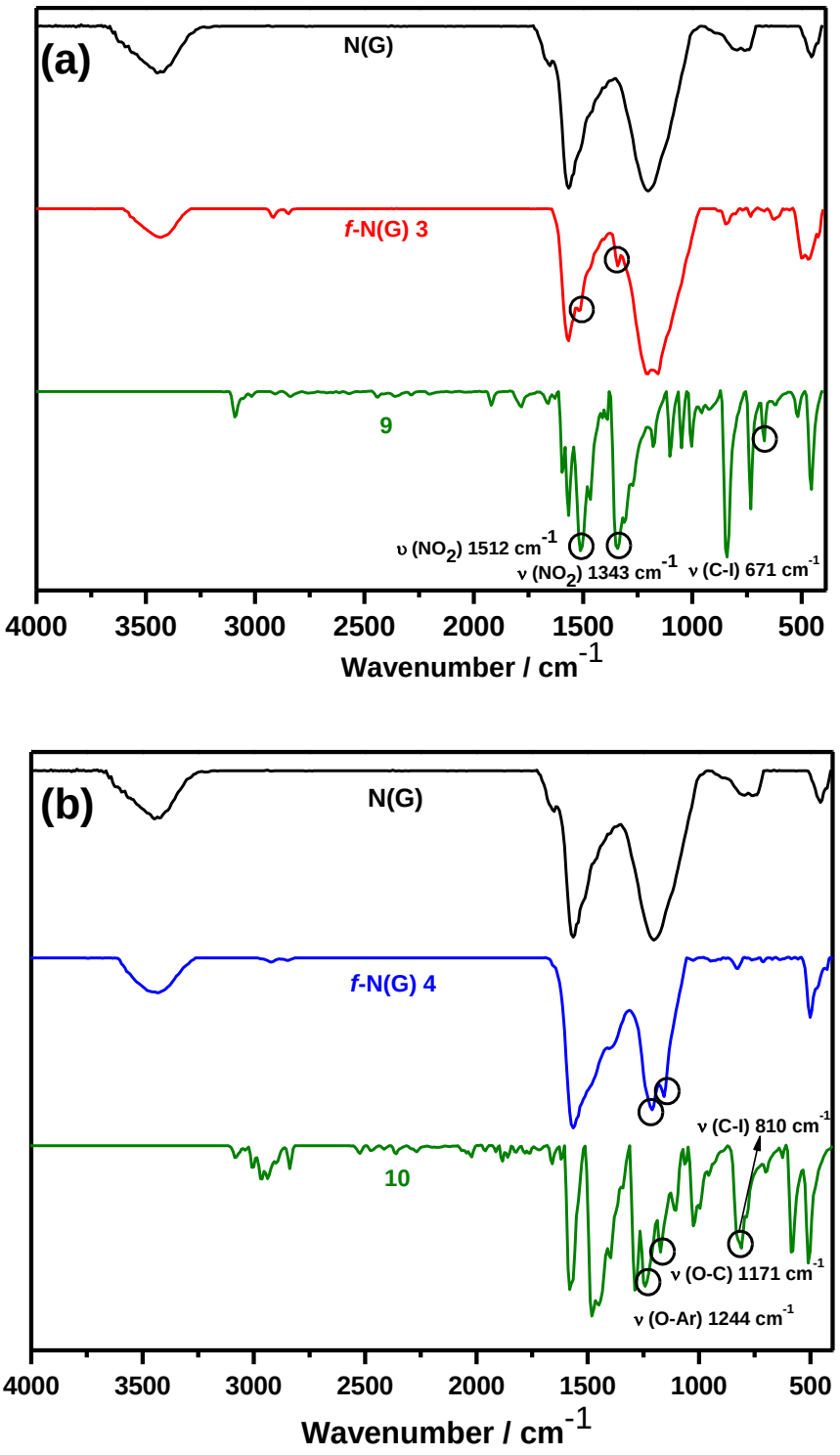


Figure S6. FT-IR spectra of (a) N(G) compared to final hybrid ***f*-N(G) 3** and the corresponding iodo-aryl derivative **9** and (b) **N(G)** compared to final hybrid ***f*-N(G) 4** and the corresponding iodine aryl derivative **10**.

Table S1. Binding energy (eV) of the core-level atoms of B(G) samples

	B1s / BE (eV)		C1s / BE (eV)				O1s BE (eV)			N1s BE (eV)		
Sample	**BC_3**	**BC_2O/BCO_2**	**sp^2C/C-B**	**sp^3C**	**C-O/C-N**	**C=O**	**O=C**	**O ad.***	**O-C**	**N-C**	**NH_2****	**NO_2**
B(G)	191.1 (45)	192.7 (55)	284.6 (70)	285.5 (21)	286.3 (9)	-	530.7 (19)	532.6 (56)	533.9 (25)	-	-	-
***f*-B(G) 1**	190.9 (55)	192.7 (45)	284.6 (62)	285.5 (25)	286.6 (11)	288.5 (2)	531.4 (30)	533 (42)	534 (28)	-	-	-
***f*-B(G) 2**	190.9 (57)	192.7 (43)	284.7 (66)	285.7 (20)	286.8 (11)	288.4 (3)	531.6 (58)	-	533.1 (42)	399.6 (43)	400.1 (36)	405.9 (21)

* This signal is due to the adsorbed oxygen species.[3]

** This signal is associated with the reduction of the nitro group to amine group by X-ray irradiation in the XPS measurement.[4]

Table S2. Composition of atomic ratios of B(G) samples determined from the XPS survey spectra.

Sample	Core	Atomic (%)
B(G)	**C1s**	82.64
	B1s	8.62
	O1s	8.74
***f*-B(G) 1**	**C1s**	84.8
	B1s	2.14
	O1s	13.06
***f*-B(G) 2**	**C1s**	74.56
	B1s	1.71
	O1s	21.52
	N1s	2.21

Table S3. Raman G shift based on TGA functionalization in ***f*-N(G)** hybrids **3-4**.

Sample	TGA weight loss (%)	RAMAN G band (cm^{-1})
N(G)	10.3	1586
***f*-N(G) 3a**	30.7	1588
***f*-N(G) 3b**	48	1597
***f*-N(G) 4a**	21.3	1584
***f*-N(G) 4b**	39.1	1581

Table S4. Binding energy (eV) of the core-level atoms of N(G) samples

	C1s / BE (eV)				O1s BE (eV)			N1s BE (eV)			
Sample	**sp^2C**	**sp^3C**	**C-O/C-N**	**C=O**	**O=C**	**O ad.***	**O-C**	**Pyridinic N**	**Pyrrolic N**	**Quaternary N**	**NO_2**
N(G)	284.8 (68)	-	286.2 (23)	288.0 (5)	531.5 (38)	532.6 (33)	533.8 (32)	398.2 (49)	400.2 (36)	401.8 (15)	-
***f*-N(G) 3a**	284.8 (74)	-	286.2 (17)	287.8 (6)	531.4 (32)	532.6 (36)	533.8 (32)	398.2 (28)	400.1 (40)	401.8 (18)	406.2 (14)
***f*-N(G) 3b**	284.8 (72)	-	286.2 (22)	287.8 (6)	531.4 (39)	532.6 (33)	533.8 (28)	398.2 (20)	400.1 (43)	401.8 (18)	406.1 (19)
***f*-N(G) 4a**	284.8 (74)	285.2 (4)	286.2 (18)	287.8 (4)	531.4 (39)	532.6 (37)	533.8 (24)	398.2 (33)	400.1 (41)	401.8 (26)	-
***f*-N(G) 4b**	284.8 (70)	285.2 (6)	286.2 (19)	287.8 (5)	531.4 (41)	532.6 (33)	533.8 (26)	398.2 (31)	400.1 (46)	401.8 (23)	-

* This signal is due to the adsorbed oxygen species.

Table S5. Conductivity values of B(G) and N(G) samples.

Sample	Conductivity (S/m)
B(G)	1.15
***f*-B(G) 1**	1.10
***f*-B(G) 2**	0.52
N(G)	357.14
***f*-N(G) 3a**	71.94
***f*-N(G) 3b**	18.15
***f*-N(G) 4a**	48.08
***f*-N(G) 4b**	20.51

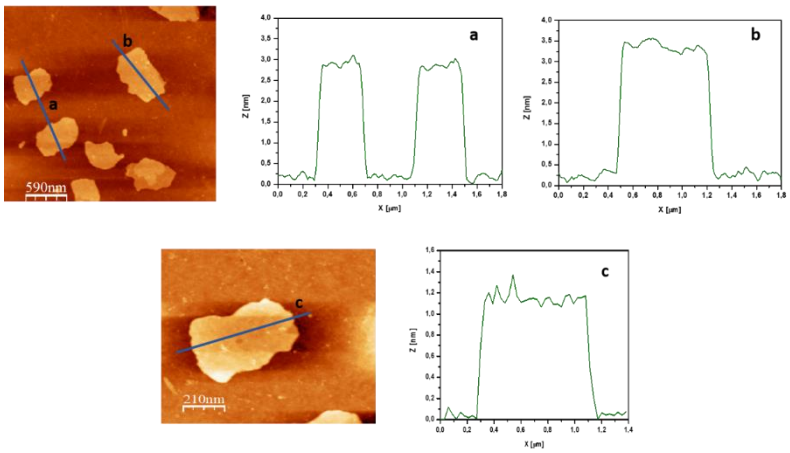


Figure S7. AFM topographic images of B(G) starting material on a SiO_2 surface with height profiles showing a height increment of ca. 3 nm (a-b) and ca. 1.2 nm (c).

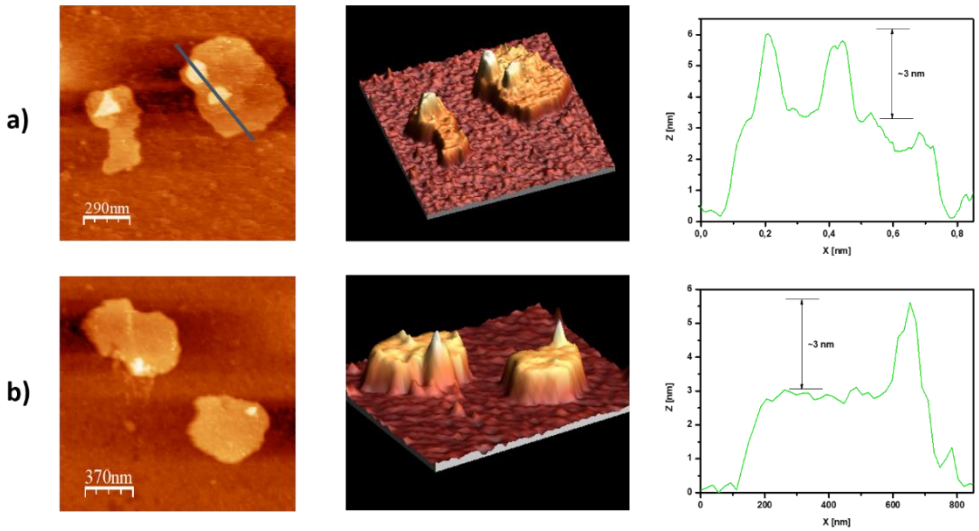


Figure S8. 2D and 3D AFM images of ***f*-B(G)** materials and height profile analysis showing an increase of ~3 nm; a) ***f*-B(G) 1** and b) ***f*-B(G) 2**.

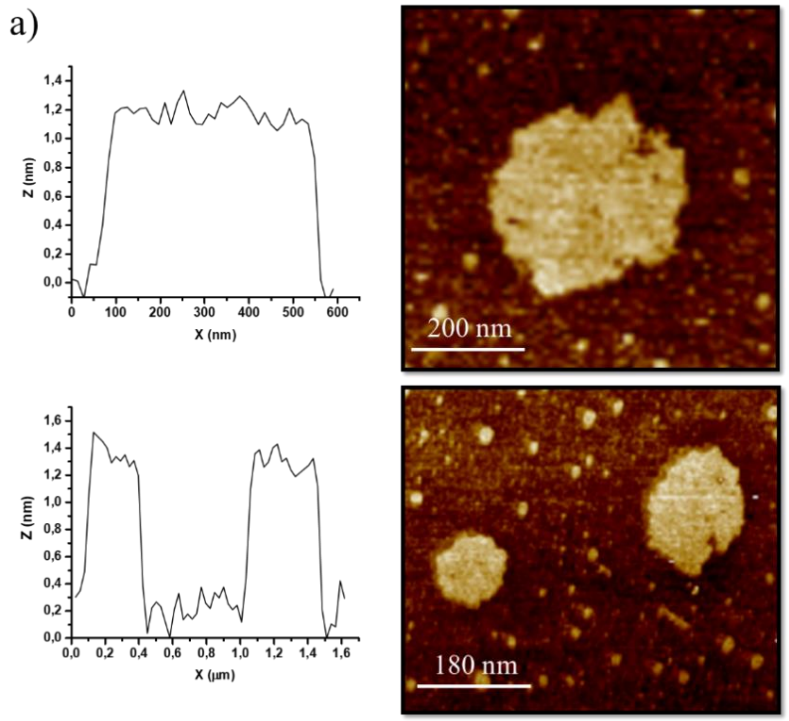


Figure S9. AFM topographic images of N(G) starting material on a SiO_2 surface with height profiles showing a height increment of ca. 1.2 nm.

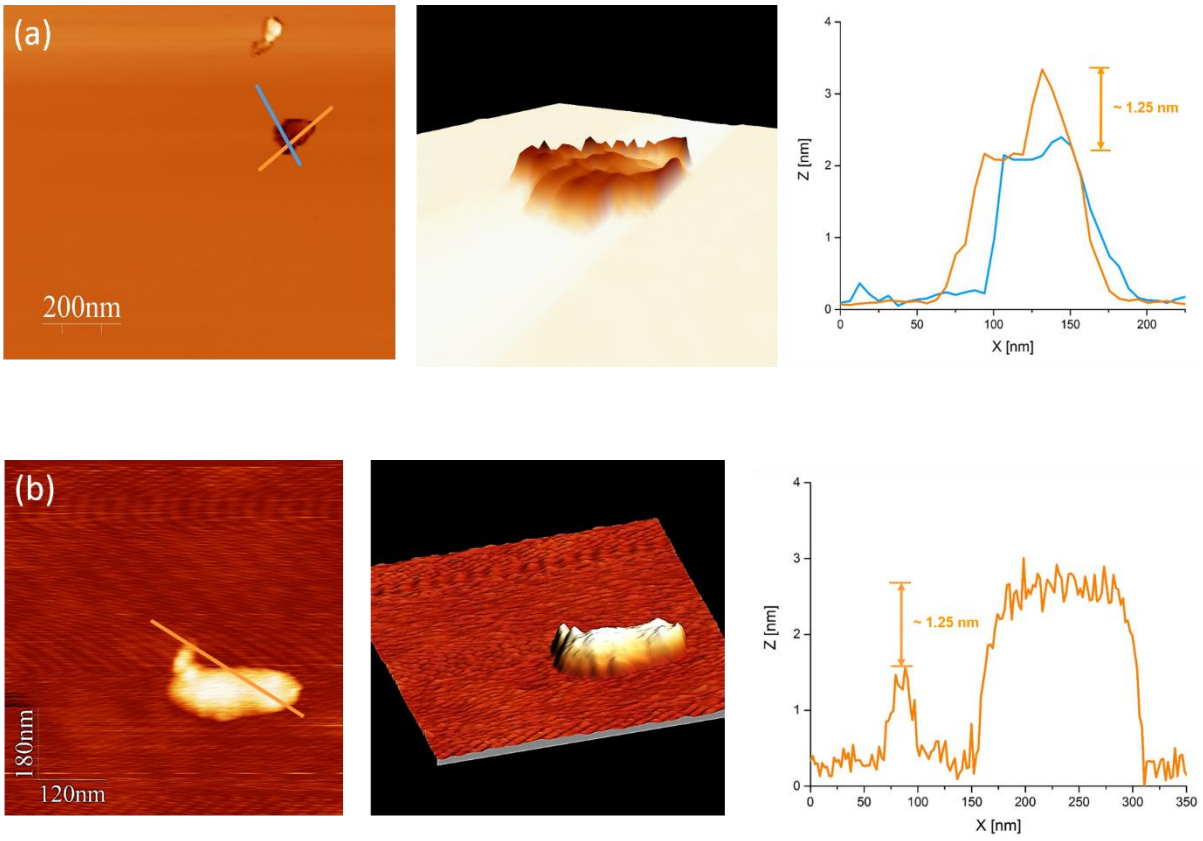


Figure S10. 2D and 3D AFM images of functionalized N(G) materials and height profile analysis showing an increase of~1.25 nm. (a) ***f*-N(G) 3b**; (b) ***f*-N(G) 4b**.

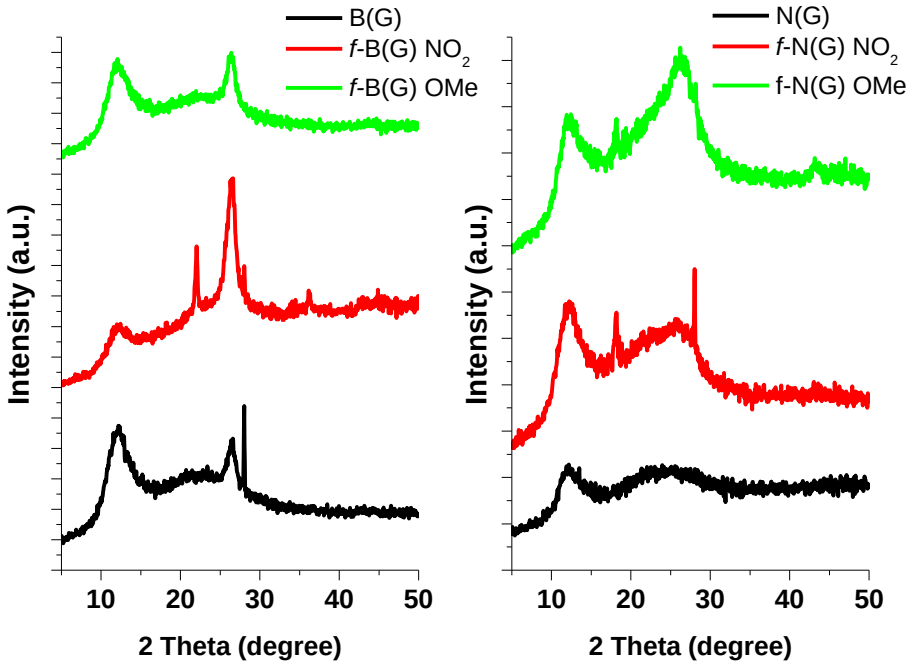


Figure S11. X-ray diffraction patterns of (left) B-doped graphene samples and (right) N-doped graphene samples.

Preparation of graphene electrodes materials:

Sample preparation

Preparation of graphene electrode: 2 mg of each sample (*f*-doped graphenes **1-4**) were dispersed in 2 mL of *N,N*-dimethylformamide (DMF) and sonicated for 10 min. After this time, the stable ink (see Figure S12) was deposited slowly by drop-coating on an acid-treated quartz substrate heated on a hotplate at 80 °C (see Figure S13). After complete drying, the corners of the graphene electrode (1x1 cm^2) were covered with conductive silver ink.

Figure S12. Inks prepared with B(G) (left) and ***f*-B(G) 2** (right) inn DMF (1 mg/mL).

Figure S13. Layer of B(G) deposited on a quartz substrate.

Hall effect measurements

To determine the sheet resistance of the samples, according to the Van Der Pauw method,[5] several measurements were made between different contacts. In each measurement, a current (I) was forced through the sample between two neighbouring contacts while the voltage (V)

was measured between the other two contacts, see Figure S14 as an example, then the following ratios R_A and R_B were calculated (equation 1 and equation 2):

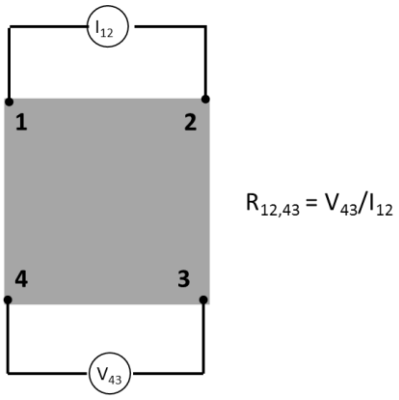


Figure S14. Example of the contact measurement for the determination of the sheet resistence.

$$R_A = \frac{R21,34+R12,43+R43,12+R34,21}{4} \qquad \text{Equation (1)}$$

$$R_B = \frac{R32,41+R23,14+R14,23+R41,32}{4} \qquad \text{Equation (2)}$$

The Van Der Pauw method related R_A and R_B with the sheet resistance (R_S) by solving equation 3

$$exp\left(-\frac{\pi \cdot R_A}{R_S}\right) + exp\left(-\frac{\pi \cdot R_B}{R_S}\right) = 1 \qquad \text{Equation (3)}$$

On the other hand, for the calculation of the Hall voltage (V_H), which relates the carrier mobility (μ_H), the major carrier concentration (n_S) and the conductivity semiconductor type (N or P), a similar procedure was followed, but the voltage was measured after appling a magnetic field perpendicular to the sample. The combination of the current flow (I) and the magnetic field caused a transverse current, thus producing a potential across the device (V_H). In addition, this

voltage was measured upon applying positive (+B) and negative (-B) magnetic field. Finally, the Hall voltage was calculated using the following equation:

$$V_H = \frac{\left(V_{24P,I13} - V_{24N,I13}\right) + \left(V_{42P,I31} - V_{42N,I31}\right) + \left(V_{13P,I42} - V_{13N,I42}\right) + \left(V_{31P,I24} - V_{31N,I24}\right)}{8} \quad Eq.4$$

Once V_H had been calculated, the mobility and sheet density of the major carrier (n_S) were obtained from equations 5 and 6:

$$n_S = \frac{I \cdot B}{q \cdot V_H} \quad Eq.5$$

$$\mu_H = \frac{V_H}{R_S \cdot I \cdot B} \quad Eq.6$$

Where I is the current applied (A), B is the magnetic field (gauss) and q the elementary charge ($1.602 \cdot 10^{-19}$ Coulombs).

All samples were connected using the sample holder SPCB-1 Spring Clip Board from Microworld and a Keithley 2450 potentiostat was used as the current and voltage source. The magnetic field used in the experiment was 0.695 T.

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