# **Electronic Supplementary Information**

# Beyond graphene oxide: Laser engineering functionalized graphene for flexible electronics

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#### Supplementary Video S1: Mechanical stability of LMod-G flexible circuit after

bending and mechanical scratching. https://youtu.be/gHsl8hvWaxM

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#### EXPERIMENTAL

# Materials

4-toluenesulfonic acid, tert-butyl nitrite, 4-aminobenzoic acid, acetic acid and diethyl ether (p.a. grade) was purchased from Sigma-Aldrich and used as received.

The graphite electrode was cut from a block of spectroscopic grade purity carbon. The deionized water, absolute ethanol, and acetone used to wash the product were acquired from Sigma-Aldrich and used without further purification.

# Preparation of diazonium salt

The 4-carboxybenzenediazonium tosylate was prepared according to a previous report.<sup>1</sup> To a solution of p-TsOH (1.425 g, 7.5 mmol) in acetic acid (12 mL), tert-butyl nitrite was slowly added (0.9 mL, 7.5 mmol). Next, 4-aminobenzoic acid (1.69 g, 5 mmol) was added in 4 steps to the reaction mixture over 1 min. The mixture was stirred for 30–40 min until TLC indicated the complete consumption of the amine (hexane/ether 1:1). After completion, the reaction mixture was precipitated by adding diethyl ether (200 mL). The precipitate was washed with diethyl ether, filtered under reduced pressure and dried under vacuum.

Mp 128 °C. IR (KBr): 2289 (N=N). 1H NMR (300 MHz, DMSO): δ 2.27 (s, 3H), 7.11 (d, J = 7.5 Hz, 2H), 7.47 (d, J = 7.5 Hz, 2H), 8.12-8.17 (m, 1H), 8.27-8.37 (m, 2H), 8.90 (d, J = 8.1 Hz, 1H). 13C NMR (75 MHz, DMSO): δ 21.14, 116.02, 125.75, 128.61, 132.75, 134.91, 135.50, 138.59, 141.12, 144.96, 162.70.

# Electrochemical exfoliation to obtain diazonium-functionalized Graphene

The graphite electrode was immersed in an electrochemical cell filled by 1 mM solution of 4-carboxybenzenediazonium tosylate in 0.1 M sulfuric acid. The electrochemical exfoliation was carried out at a stable voltage (10 V) for 1 hour using platinum wire as a counter electrode. The black-colored solution of exfoliated graphene was filtered off and washed by water, ethanol, and acetone (three times with every solvent using a centrifuge at 7830 rpm). A similar exfoliation process was realized in a drop of the same diazonium salt dispersion described above, but this time deposited on the HOPG substrate used as the electrode and graphene precursor. An Au microwire 50 micrometers diameter was used as the counter electrode. A potential difference of 10 V was applied in this system, depicted in Figure 2a, for a duration of about 20 s.

# **Device fabrication**

For the production of devices, Mod-G dispersed in an aqueous dispersion was dropcasted on the substrate of interest (glass, Kapton, graphite, silicon, and PET were investigated here). After deposition, the film was dried at 50-60 degrees Celsius for 3 hours. The Mod-G film is then placed in a laser engraver to form an electrical circuit architecture with a computer-controlled station. The laser wavelength was 405 nm with a laser power of 1 W and 100 ms pulse duration. The laser spot size was about 50  $\mu$ m diameter. The distance between two consecutive laser irradiation spots was ~72  $\mu$ m making a ~20% overlap due to the heat dissipation process. After laser irradiation, electrical contacts and pads were made with conductive Cu adhesive tape and silver paint.

# Atomic force microscopy (AFM)

For our investigation, we used a multipurpose atomic force microscope (NT-MDT). All measurements were done in the ambient environment (40% humidity) at room temperature (22°). The AFM cantilever characteristics are given below.

# Current sensing or conductive AFM (C-AFM)

The measuring scanning head with the conductive cantilever (CSG30/Pt @ tipnano) was used for conductive experiments.

The topography imaging was taken simultaneously with current, provided by BV potential applied to the sample and tip. The IV curves in point were performed in a limited range of  $\pm 1V$  due to current saturation through the tip-surface contact. For this experiment, we used a conductive substrate (HOPG).

# **Dielectric force microscopy (DFM)**

In this method, the NSG01/Pt tip was used. The images were acquired in semi-contact mode with the following parameters: resonance frequency of ca. 170 kHz, applying the AC voltage (0.4 V) to the tip (the sample was grounded). The DFM image was acquired in the second pass after lifting the tip 20 nm away from the sample.

# Kelvin probe force microscopy (KPFM)

A freshly cleaved graphite was used as a conductive electrode substrate that was grounded. A Mod-G film was formed on the graphite substrate by drop coating. The same NSG01 with Pt coated cantilever was used as for dielectric force microscopy experiments.

#### X-ray diffraction

The experimental data were obtained using XRD-6000 diffractometer based on  $CuK_{\alpha}$  radiation with a sliding beam. The operating voltage was 40 kV and current to 30 mA. The samples analyzed were GO, rGO, Mod-G, and LMod-G films deposited on glass slides.

#### Raman spectroscopy

The Raman spectroscopy analyses were performed under 785 nm excitation focused by a 50x long working distance objective on the sample with a laser power of 5 mW. The Raman signal was recorded in the backscattering geometry and analyzed with a DXR2xi Raman Imaging Microscope (Thermo Fisher Scientific U.S.A.).

# **Contact angle measurements**

The experiments were performed using a Krüss Drop Shape analyzer in laboratory conditions. For all four sample types, 3  $\mu$ L distilled water drops were deposited on the sample surface and immediately measured.

#### X-ray photoelectron spectroscopy (XPS)

Apparatus: K Alpha (Thermo Scientific); source: monochromated Al Ka (h=1486.6 eV, 400 μm spot size); pass energy: 50 and 200 eV for narrow regions and survey spectra, respectively; charge compensation: using electron and argon ion guns.

# **Gas sensing**

For this test, the device resistance was recorded after exposing the sensor to two different environments. The first one was by  $CO_2$  applied by simply breathing and exhaling on the device at a distance of ~10 cm. The reaction to ethanol vapor took place in a closed Petri dish and the experiment began when the LMod-G device was placed inside it and reacted to ethanol in the gas phase. The resistance changed almost as soon as the Petri dish was covered. We verified the reusability of the device and sensing reproducibility for over a week period.

# Bending tests

Bending tests were carried out by direct mechanical deforming the LMod-G devices deposited on a polyethylene terephthalate (PET) substrate at 180° bending angle. The resistance was measured before and after bending showing a reproducible recovery after the device was relaxed. Over 50 manual bending cycles were performed without any degradation of electrical conductance. An LMod-G film on Kapton was also used for the mechanical stability test, bent at 90° and operated constantly for over 30 days without fail.



Fig. S1 (a) Photograph of the electrochemical cell during exfoliation of a graphite electrode. (b) Current evolution during the electrochemical exfoliation of the graphite electrode at a potential of 10 V during 1h. (c) Schematics showing the changing in the carbon oxidation state from graphene to Mod-G, and from Mod-G to LMod-G involving reduction and oxidation steps, respectively.



Fig. S2 AFM topography of an electrochemically exfoliated HOPG electrode showing blisters and an aggregate marked by arrows. The aggregate was the one where the IV curve shown in Fig. 3e was taken.



Fig. S3 (a) Topography and (b) conductivity images of laser-reduced GO. (c) IV (nano) characteristics of rGO on glass obtained from the X mark location in (b).



Fig. S4 IV (macro) characteristics of LMod-G and Mod-G obtained from the same film deposited on PET but with and without laser irradiation. The slope value for Mod-G is at the noise level of the instrumentation readout about zero current.



Fig. S5 FTIR spectra acquired from Mod-G on a Kapton substrate and a laser-irradiated region (LMod-G). The spectrum from the Kapton substrate is included as a reference showing the main bands from polyamide.<sup>2</sup> The bands marked by arrows in LMod-G correspond to the changes induced in the sample after laser irradiation which indicates the removal of the aryl group.<sup>2</sup>

IR spectra were acquired on the Agilent Cary 630 FTIR spectrometer in ATR mode from the samples Mod-G and LMod-G on a Kapton substrate (2000 scans per sample). The raw spectral data were processed using OMNIC software package *via* the sequential subtraction of pristine Kapton spectrum, baseline correction, and smoothing.

The spectra show differences between Mod-G and LMod-G regions. In particular, the appearance of vibrational bands from O-H in the range 3500-3600 cm<sup>-1</sup> comes from the 4-carboxyphenyl functional groups in Mod-G. The second characteristic peak from C=O bond at 1700 cm<sup>-1</sup> overlaps with intrinsic vibration bands from Kapton and therefore cannot be differentiated from the background. The peaks associated with C-H bonds from hydrogenated defects in graphene around 2850-2950 cm<sup>-1</sup> and C=C vibrational bands near the 1500-1600 cm<sup>-1</sup> are also visible. The laser treatment of mod-G led to the cleavage of C-C bond between graphene sheets and aryl groups evidenced by the disappearance of the characteristic signal of O-H bonds. Particularly important is the change of intensity ratio between C=C graphene-related vibrational bands (1500-1600 cm<sup>-1</sup>) and C=O bonds (1700 cm<sup>-1</sup>). These changes can be associated with the decreasing of C=O concentration due to the removal of 4-

carboxyphenyl moieties after laser irradiation.



Fig. S6 XPS data. (a) Survey spectrum of Mod-G film on PET and (b) high-resolution spectra of C1s and O1s regions before laser irradiation, respectively. (c) Survey spectrum of Mod-G and (d) spectra for the C1s and O1s regions after laser irradiation (LMod-G).

The survey spectra displayed in Fig. S6a,c exhibit the main peaks C1s and O1s centered at 285 and 533 eV, respectively. The C/O atomic ratio is 3.3 for the Mod-G and decreases to 2.8 for LMod-G material. In addition, a low-intensity N1s peak is noted in Fig. S6a and assigned to the reaction of the diazonium with graphene that results in the formation of -N=N- groups. The N1s peak in Fig. S6a is centered at 399.6 eV and has a component at 401.5 eV due to possible protonation.<sup>1</sup> The high-resolution C1s and O1s spectra of Mod-G are shown in Fig. S6b. C1s is fitted with four components due to C=C/C-C/C-H, C-O, O-C=O and a small shakeup satellite centered at 284.6, 286.7, 288.7, and 290.7 eV, respectively. The O1s narrow region is fitted with two peaks centered at 531.7 and 532.8 eV assigned to C=O and C-O, respectively (Figure S6b). Interestingly, after laser irradiation, it is worth to notice the complete change in the shapes of the high-resolution C1s and O1s peaks (Figure S6d). The C1s narrow region is fitted again with the same components but showing completely different peak intensity ratios. The O-C=O peak component is slightly more intense than that of C-O due to the carboxylic acid groups from graphene. In addition, the main peak is guite intense with a C-C/C-O ratio of 7.8, much higher than the theoretical ratio of 3 for pure PET. This higher peak intensity ratio accounts for the presence of graphene. It is also interesting to note the drastic attenuation of the C-O contribution to the C1s peak. It is concomitant with the decrease in the O1s(C-O)/(O1s(C=O) intensity ratio from 2.1 to 1.1, close to the expected theoretical ratio for pure PET. This observation confirms that the laser processing of Mod-G induces the full cleavage of 4-carboxyphenylene groups initially attached to the graphene surface during the electrochemical exfoliation and functionalization step.



Fig. S7 (a) Topography and (b) cross-section analysis of the interface between Mod-G drop from the supernatant solution and the HOPG substrate. The cross-section shown in (b) was made along the dashed line in (a). At the edge of the drop, the "coffee ring" region, the supernatant Mod-G made a 25 nm film on HOPG.

In Fig. S7a, we see the AFM topography image of an interface between Mod-G and the HOPG substrate. The thickness of the film is about 25 nm as deduced from the cross-section analysis shown in Fig. S7b. This film could be a result of over functionalization and crosslinking of aryl groups from radicals in the solution during film formation.<sup>4</sup>



Fig. S8 (a) Raman spectra from Mod-G, and laser-irradiated Mod-G (L-Mod-G). The coffee ring and

blank glass<sup>5</sup> spectra were obtained by averaging from the Raman hyperspectral imaging analysis of Mod-G deposited on glass. The glass spectrum intensity was arbitrarily scaled to use as a reference. (b) Raman intensity maps of the glass peak at 1387 cm<sup>-1</sup> and (c) the G band at 1598 cm<sup>-1</sup>. (d) Optical microscopy image of the region analyzed by Raman imaging around the coffee ring made by the drop deposition of Mod-G.



Fig. S9 (a) Sketch of the four types of graphene materials studied by Raman spectroscopy and X-Ray diffraction, both graphene oxide and Mod-G with and without laser irradiation. (b) Raman spectra comparison for films made of pristine (without laser irradiation) graphene oxide (GO), Mod-G, and laser-reduced GO. Raman spectra of (c) Mod-G and (d) laser-irradiated Mod-G (LMod-G). The different peaks shown in the spectra were fitted with Voigt functions following the work of Claramunt *et al.*<sup>6</sup> Albeit the large error bars in the peaks' position determination of D", there is a clear decrease in D\* that is reported as a signature of reduction. The rest of the peaks have similar peak positions. The small change in D peak position could be related to doping changes in Mod-G after laser irradiation<sup>7</sup> although given the fit uncertainty we refrain from a further interpretation of this minute change. As a reference of purely sp<sup>2</sup> hybridized carbon, the Raman spectrum from single-layer graphene is included in (d).



Fig. S10 The contact angle of graphene materials here investigated, before (GO, Mod-G) and after laser treatment (rGO, LMod-G)



Fig. S11 (a) Photographs of the laser-irradiated Mod-G used in a flexible circuit powered by a solar cell. The circuit was running 24/7 for over a month, disconnected only to test the current stability. The stability of the flexible conductor was evaluated with an external power supply at 3V to light the LED in the picture. (b) From over two dozen individual measurements of the current over a period of several days the device showed a stable current of (344±6) µA with the stability of over 98%.



Fig. S12 (a) IV characteristics of a flexible LMod-G/PET device under bent and relaxed conditions as shown in (b). The device shows only an insignificant change in conductance after being in contact with water as shown in (c). The conductance recovers to its initial state after the device dry. (d) Optical microscope image of the silver contact used in the flexible circuit after bending tests. The failure of the device was due to this contact that once remade allowed the circuit to work again. This shows the superior mechanical stability of LMod-G with respect to conductive silver inks and pastes widely used in flexible electronics.



Fig. S13 100 mL bottles with water dispersions of electrochemically-exfoliated graphene obtained in the presence of diazonium salt (Mod-G) and without it (graphene) at different time intervals showing the long-term water dispersibility of Mod-G. Except for the presence of diazonium salt, both dispersions were obtained under the same conditions.

Chemiresistor material	Detected gas	ΔR/R, %	DOI, figure
LMod-G	Ethanol	16.2	this work*, Fig. 6d
Inkjet-printed rGO/PET	Ethanol	9.5	<sup>8</sup> , Fig. 3b
SWNT	Ethanol	0.3	<sup>9</sup> , Fig. 3d
MWCNT-polymer	Ethanol	5.5	<sup>10</sup> , Fig. 9

\*LMod-G value is based on 9 different days measurements arithmetical mean with a deviation of  $\pm 0.6\%$ .

Table S2:  $CO_2$  sensitivity comparison. In our breathing experiments, we consider the  $CO_2$  in exhaled breath from the experiments shown in Fig. 6d and Fig. 6e.

Chemiresistor material	Detected gas	ΔR/R, %	DOI, page
LMod-G	CO <sub>2</sub>	15.6	this work*, Fig. 6e
RGO	CO <sub>2</sub>	3.9	<sup>11</sup> , Fig. 9d
PEI-PANI	CO <sub>2</sub>	9	<sup>12</sup> , Fig. 6
SWNT	CO <sub>2</sub>	2.2	<sup>9</sup> , Fig. 3d

\*LMod-G value was obtained from the arithmetical mean of 17 experiments performed on different days with a deviation of  $\pm 0.4\%$ .

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