

SUPPORTING INFORMATION

Effects of graphene defects on gas sensing properties towards NO₂ detection

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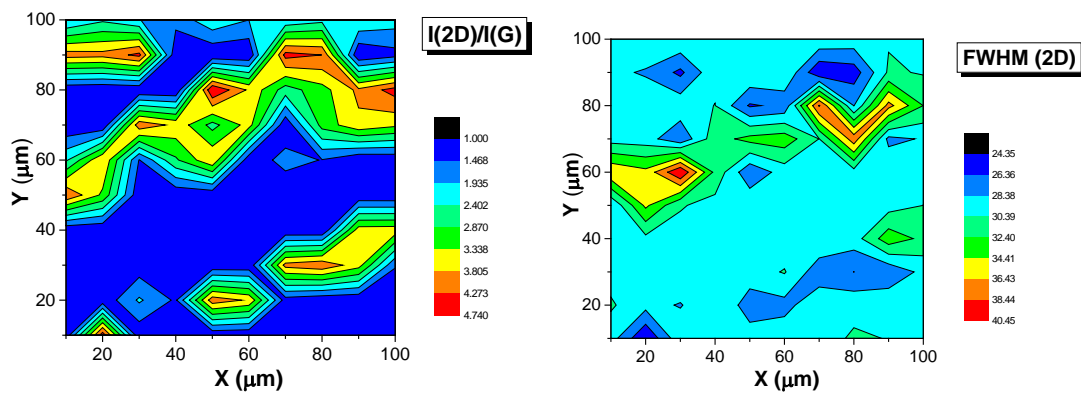
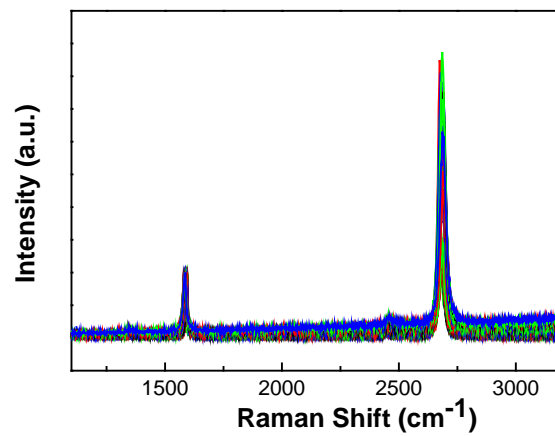
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Raman characterizations

As reported in the main text, the scanned area on the samples prepared through Mechanical Exfoliation (ME), Chemical Vapor Deposition (CVD) and Liquid Phase Exfoliation (LPE) was equal to $100 \times 100 \mu\text{m}^2$ and the distance between two subsequent spectra was set as $10 \mu\text{m}$.

ME-Gr



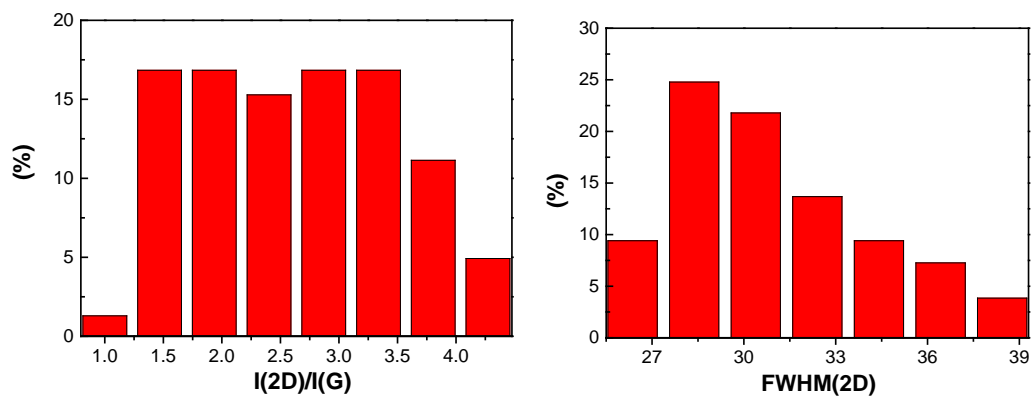
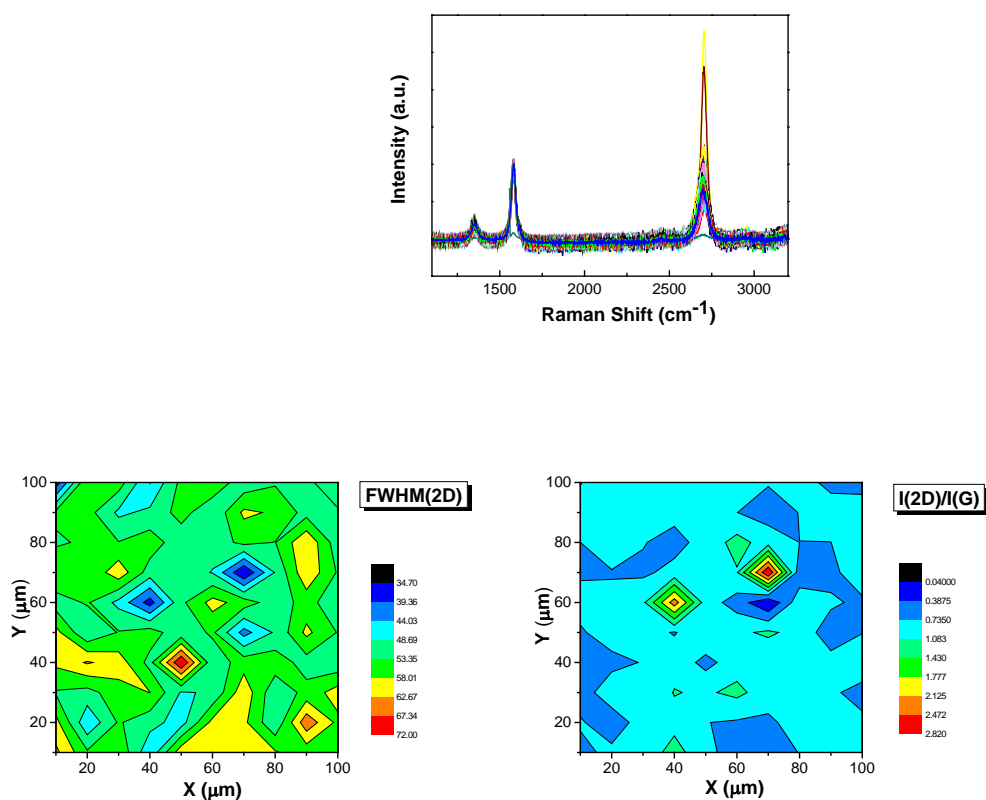


Figure S1. (a) Collection of 100 Raman spectra acquired on ME-Gr. (b) Map of FWHM(2D) and (c) histogram of the distribution associated to the map over the scanned area. (d) - (e) I(2D)/I(G) map and relative histogram, respectively.

CVD-Gr



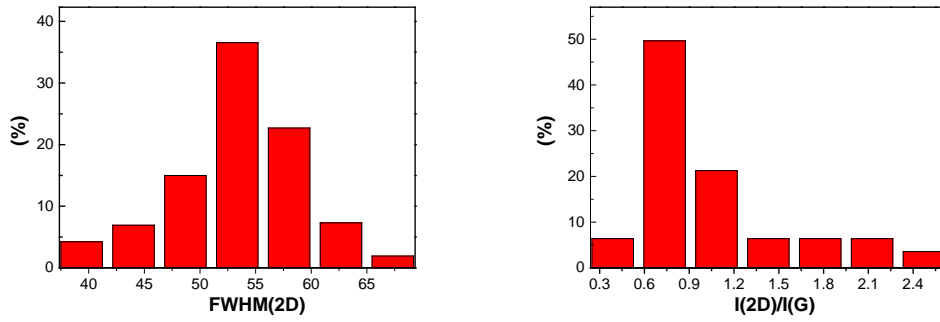


Figure S2. (a) Collection of 100 Raman spectra acquired on CVD-Gr. (b) Map of FWHM (2D) and (c) histogram of the distribution associated to the map over the scanned area. (d) - (e) I(2D)/I(G) map and relative histogram, respectively.

LPE-Gr

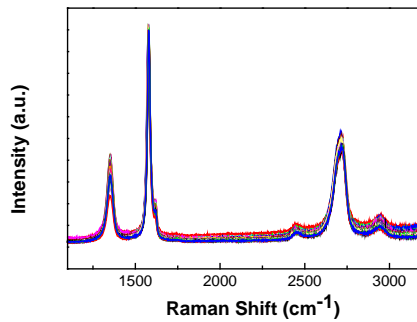


Figure S3. Collection of 100 Raman spectra acquired on the area of LPE-Gr sample.

With respect to the ME-Gr and CVD-Gr samples, FWHM (2D) and I(2D)/I(G) maps as well as the associated histograms of the distributions cannot be computed. In fact, as revealed by the Raman spectra (**Figure S3**), the 2D band of all spectra is not constituted of a single Lorentzian. Hence, a single Lorentzian is not a proper fit so that both the full width at half maximum and the intensity of 2D cannot be defined.

Realization of Mechanical Exfoliated Graphene based chemi-resistors

The Si/SiO₂ sample with deposited graphene flakes on top were washed in acetone for 2 min and then rinsed in isopropanol. The sample was baked at 120°C for 2 min aiming to the removal of solvent residues before depositing a thin film (160 nm) of poly(methyl methacrylate) (PMMA) A4 (2:1) by spin coating. Prior to patterning it, the sample was hard-baked at 170°C for 7 min in order to strengthen the resist structure.

By means of e-beam lithography, pattern of markers and electrodes was defined, further followed by metallization with Ti/Au thin film (5 nm/50 nm) in an electron-beam evaporator (Kenosistec Inc). The lift-off step consisted of keeping the sample in acetone overnight.

Differential method applied to the dynamic sensors behavior

In order to strengthen the trend of the rate demonstrated in the main text for the various devices, the differential method introduced in our previous work⁽¹⁾ was applied to the dynamic sensor responses. **Figure S4** reports the differential current, calculated during each gas pulse, for each device mentioned in the main text.

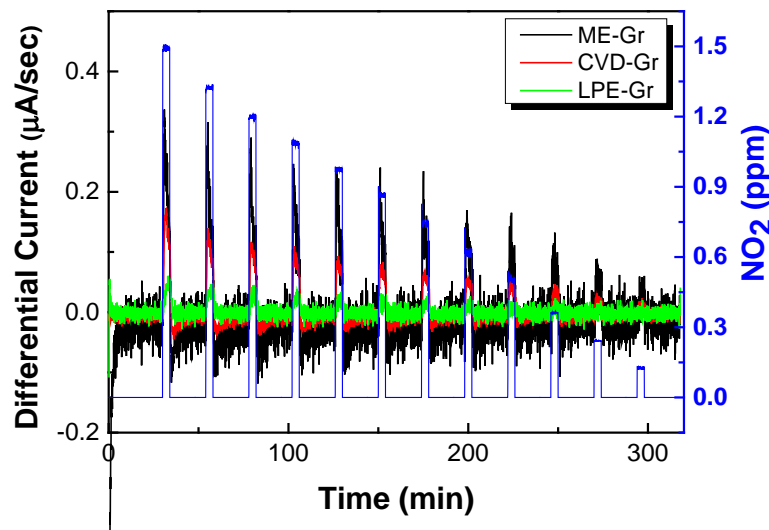


Figure S4. Differential currents of the dynamic behaviors upon exposure to sequential NO₂ different concentrations ranging from 0.12 up to 1.5 ppm. The graphs refer to the cycles reported in Figure 5 of the main text.

For each step, the ratios between the maxima of intensity (ME-Gr/CVD-Gr and CVD-Gr/LPE-Gr) result to be roughly equal to 2, as mentioned in the main text (**Table 1**). At low gas concentrations, owing to the fact that the devices are led quite close to the limits of working conditions, the signal appears indistinguishable from the noise. Notwithstanding, the slope trend discussed in the main text for the first two steps still keeps valid for each pulse.

REFERENCES

1. Ricciardella, F.; Massera, E.; Polichetti, T.; Miglietta, M. L.; Di Francia, G. A Calibrated graphene-based chemi-sensor for sub-ppm NO₂ detection operating at room temperature. *Appl. Phys. Lett.* **2014**, 104, 183502.