The Role of Edge Defects in Liquid Phase Exfoliated and Chemical Vapor Deposited Graphene for NO_2 Detection

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The attraction of graphene for the sensing field has been widely demonstrated in the literature, mostly due to its large theoretical specific surface area (2630 m^2/g) and to the other unique and supreme properties allowing detection down to a single molecule [1-2]. Since the sensor and, particularly, the gas sensor field is continuously running up towards new horizons, one of the ongoing challenges is to detect toxic gases at extremely low concentrations, especially for devices working in environmental conditions.

It is well known that the graphene edges exhibits a higher reactivity compared to the planar surface [3-5]. Herein, we report on the study of the sensing properties of graphene prepared by two different routes, Liquid Phase Exfoliation (LPE) and Chemical Vapor Deposition (CVD), showing that the graphene morphological structure can play a fundamental role in detecting concentrations at level of few parts-per-billion (ppb) of NO_2.

LPE graphene was synthesized by mild sonication of natural powdered graphite (Sigma-Aldrich, product 332461) in N-methyl-pyrrolidone (NMP) at 10 mg/ml for 3 h, removing thicker graphitic platelets by centrifugation at 500 rpm [6].

CVD graphene was grown on a Cu film of 500 nm bringing the temperature gradually up to 900 °C as described in [7]. Both materials were characterized by Raman spectroscopy (Renishaw inVia Reflex, λ=514.5 nm) and Atomic Force Microscopy (AFM) (Ntegra Spectra microscope) (Figures 1). LPE graphene was also characterized by Transmission Electron Microscopy (TEM) (FEI TECNAI G12 Spirit-Twin operating at 120 kV). The Raman analysis displayed an LPE material composed by flakes with number of layers equal to or less than five with the presence of some defects [6]. TEM and AFM characterizations confirmed the presence of many edges. Raman spectra on CVD graphene showed a nearly single layer material, whereas the AFM topography highlights a higher edges density in LPE material with respect to CVD graphene sheet. To verify the role of the edges in the sensing behavior, the performances of chemi-resistors, realized with both kinds of materials, were compared.

The device based on LPE material (Device 1) was realized by drop casting few microliters of the suspension on alumina substrates with gold interdigited electrodes (IDEs) (Figure 2) whereas CVD graphene-based device (Device 2) was obtained transferring the material onto lithographic IDEs (Figure 3). The chemi-resistors were tested in a Gas Sensor Characterization System towards NO_2 for 10 min in wet N_2 with a flow of 500sccm, setting T=25°C and relative humidity at 50%, respectively.

Device 1 provided a conductance variation equal to 6% upon exposure 350 ppb of NO_2 (Figure 2) whereas an appreciable conductance variation (0.85%) for Device 2 was recorded upon 480 ppb (Figure 3). The limits of detection, extrapolated from the calibration curves (Figures 4-5), are roughly equal to 50 ppb and 600 ppb for Device 1 and 2, respectively.

The behavior of the two devices towards the NO_2 definitively testifies the influence of flakes morphology on the interaction mechanism between graphene and analyte molecules.

References

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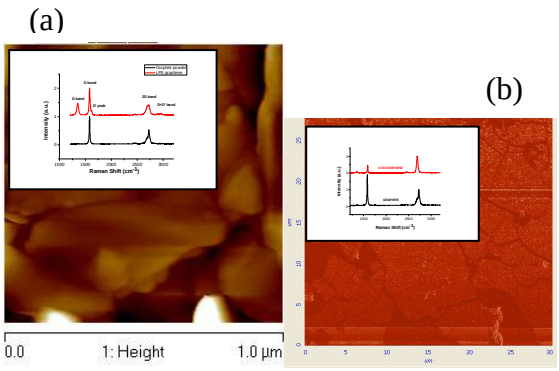

Figure 1: AFM images of LPE (a) and CVD graphene. Insets: Raman spectra of graphene (red curves) and graphite (black curves).

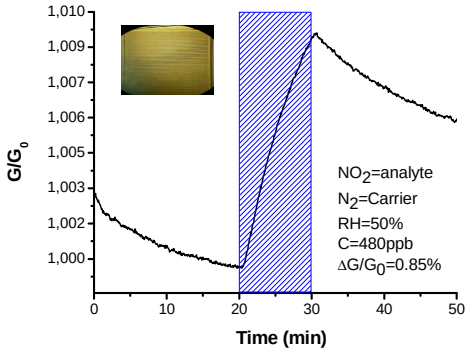

Figure 2: Conductance response of the device based on LPE graphene towards NO_2, where G_0 is the unperturbed conductance at the gas inlet. Inset: image of the gold IDEs on alumina.

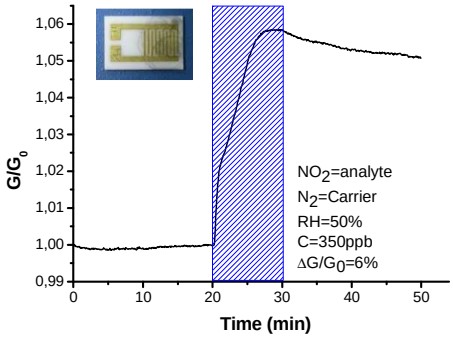

Figure 3: Conductance response of the device based on CVD graphene towards NO_2, Inset: image of the IDEs designed by lithography.

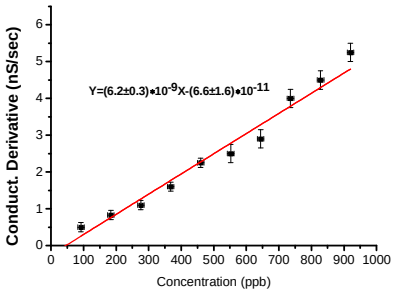

Figure 4: Calibration plot of chemi-sensor based on LPE graphene.

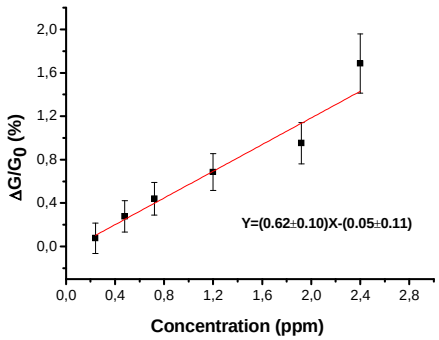

Figure 5: Calibration plot of chemi-sensor based on CVD-grown graphene.