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Chemically exfoliated graphene detects NO_2 at the ppb level

M. L. Miglietta*, E. Massera, S. Romano, T. Polichetti, I. Nasti, F. Ricciardella, G. Fattoruso and G. Di Francia

ENEA Centro Ricerche Portici, Piazzale E. Fermi 1, 80055 Portici (NA), Italy

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Abstract

The high sensitivity of graphene to the adsorption/desorption of gas molecule, is at the very beginning of its exploitation. This sensitivity relies on the two-dimensional nature of graphene allowing a total exposure of all its atoms to the adsorbing gas molecules, thus providing the greatest sensor area per unit volume. Indeed several technological limits weigh on the synthesis and manipulation of the material for the device fabrication. Herein a simple approach to fabricate conductometric sensors based on chemically exfoliated natural graphite is presented. The devices were tested upon sub-ppm concentrations of NO_2 in environmental conditions and show the ability to detect this toxic gas down to few ppb at room temperature.

Chemical sensor; graphene; air pollutant

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1. Introduction

One of the most extraordinary properties of the graphene is the high sensitivity to the adsorption/desorption of gas molecule. The ability to detect the presence even of a single interacting molecule has been proven for the graphene flake [1]. Nevertheless, due to the complexity of the entire process, starting from the graphene synthesis and/or isolation up to the introduction into the proper device architecture, the fabrication of the single graphene flake based chemical sensor is still challenging. To date, indeed, several works report on the fabrication of gas sensor devices that employ, as sensing layers, a much more easily manageable material such as the reduced graphene oxide sheets [2,3,4]. Chemically reduced graphene oxide has been studied as sensing layer for gases like NO_2, NH_3 but also for vapors

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* Corresponding author. Piazzale E. Fermi 1, 80055 Portici (NA), Italy, Tel.:+39 081 7723232, fax:+39 081 7723344.
E-mail address: : mara.miglietta@enea.it.

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such as acetone, methanol and several warfare agents simulants showing the capability to detect these analytes in ppm or, in some cases, down to the parts per billion concentrations [2-5]. However, these graphene based sensors were hardly tested in real environmental conditions, i.e. wet air at room temperature.

Herein a simple chemiresistor device based on graphene derived by the chemical exfoliation of natural graphite is described. Graphene suspensions were prepared by different procedures and the resulting materials tested as chemiresistive sensing layers. The devices were tested under environmental conditions towards NO_2 showing that the change in the device conductance upon NO_2 exposure is very high and that the sensor performances are fairly reproducible. Due to the low device noise, it was possible to estimate a detection limit as low as tens of ppb, consistent with the best performance observed in the few-layers devices [1].

2. Experimental

Stable suspensions of graphene were obtained by exfoliation of graphite with organic solvents. Different graphene dispersions were prepared by mild sonication of a natural powdered graphite (Sigma-Aldrich, product 332461) in N-methyl-pirrolidone (NMP) or N,N-dimethylformamide (DMF) at 10 mg/ml for 3 hours. Thicker graphitic platelets were removed by centrifugation. In this work two extreme centrifugation rates were used in order to assess the effect of the concentration and flake size on the resulting sensing layer: 500 rpm and 13000 rpm respectively. The mean size of the dispersed flakes were measured by the Dynamic Light Scattering technique with a Zetasizer Nano (Malvern Instruments).

Few microliters of these dispersions were deposited by drop-casting onto alumina transducers with Au interdigitated electrodes. The sensor devices were exposed to a flow of 350 ppb of NO_2 for 10 minutes in different carrier gas: dry and humid N_2, dry and humid air, with constant flow of 500 sccm, at 22°C. The electrical characterisation of the sensors was performed using a volt-amperometric technique, at constant bias. In such a system (Kenosistec equipment), the device is located in a stainless steel testing chamber placed in a thermostatic box. The testing chamber was provided of an electrical grounded connector for bias and conductance measurements [6]

3. Results and discussion

The mean particle size of graphene sheets dispersed in NMP fall off dramatically from 198±2 nm to 67±1 nm with increasing rotation rate from 500 rpm to 13000 rpm. In fact, the centrifugation rate affects the composition of the final suspension; the concentration, decreases monotonically with the rotation rate and besides, the flake dimensions decreases [7]. A similar trend was observed for the dispersions made in DMF but in this case, the mean particle size was pretty larger (from 440 to 160 nm). Such results are also confirmed by TEM measurements. The TEM image of a graphene films made from a NMP suspension centrifuged at 500 rpm shows that the suspension is mainly composed by few layer flakes and sparse thick graphitic fragments (fig. 1).

Graphene based chemical sensor devices were fabricated by drop-casting few microliters of the colloidal graphene dispersions onto Au interdigitated electrodes printed on an alumina substrate. Every device was tested against the same concentration of NO_2 and all of them has shown a marked response upon exposure with a sharp increase of its conductance and a slow recovery. Due to this incomplete recovery after sensing signal and to a slightly different sensing performance from device to device, a conventional signal processing could be misleading, giving unrepeatable responses. Hence, in order to compare the kinetics behavior among different devices and sensing cycles we show in figure 2 a plot of the normalized signals $((S-S_0)/(S_{max} - S_0))$ vs time of devices prepared from a DMF suspension of graphene in different carriers. The response kinetics during the analyte exposure is nearly alike in all the testing environments. A slight difference can be observed in the recovery behavior. In fact, the presence of moisture seems to favor the desorption of NO_2 molecules, restoring the conductance. Actually, desorption kinetics is much slower than the adsorption, as it was already observed for other graphene based chemical sensors and, generally, for room temperature operating solid state sensor.

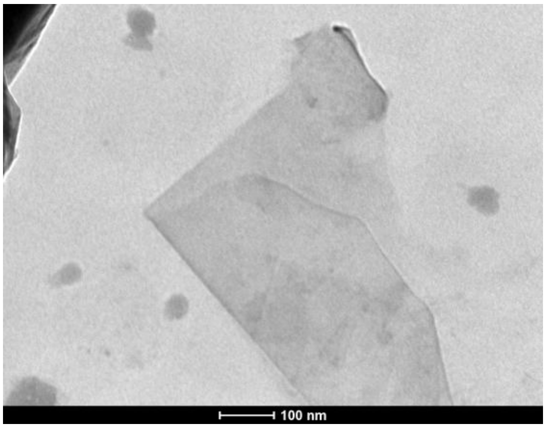

Fig. 1: TEM image of graphene flakes obtained by exfoliation with NMP.

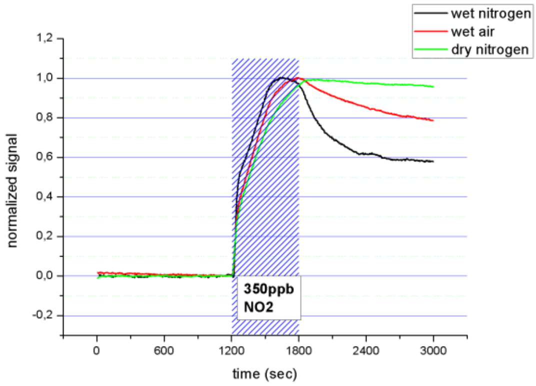

Fig 2: Normalized conductance response $((S\text{-}S_0)/(S_{max} - S_0))$ kinetics upon exposure to 350 ppb of NO_2 in dry nitrogen, wet nitrogen and wet air. Sample is exposed to the analyte in a volume of 0,4 L with a flow of 500sccm at 22 °C. The device is DC biased at 10V.

4. Conclusions

In this work a simple approach to the fabrication of a chemiresistor device, based on chemically exfoliated graphene, was illustrated. Sensors characterization showed very interesting results, in line with those reported in literature for the reduced graphene oxide based chemical sensor. Our preliminary findings are a promising starting point to investigate this material as conductometric layer for gas sensing at room temperature in environmental conditions.

Acknowledgements

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