Inkjet Printed Graphene-Based Chemiresistive Sensors to NO_2

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Abstract. In this work, the possibility of manufacturing chemiresistive gas sensing devices by inkjet printing different LPE (Liquid Phase Exfoliation) graphene suspensions, formulated in standard organic solvents or aqueous mixtures, on rigid and flexible substrates has been studied. The sensing film has been obtained by printing a different number of graphene layers, depending on the specific ink/substrate system. The device performances have been investigated upon exposure to different concentrations of NO_2 at ambient pressure and temperature, addressing the device-to-device variation as function of the number of printed layers and the base conductance.

Keywords: Liquid phase exfoliation graphene · Ink-jet printing · Aqueous dispersion · Chemiresistive gas sensors

1 Introduction

Graphene is a material with surprising properties, that catalyzed the attention of the scientific community in the last years for its potential applications in different fields, from electronics to sensors.

Several techniques have been investigated for the graphene fabrication. With respect to mechanical exfoliation methods [1], which are not suited for the industrial scalability though providing highest quality material, the processes Chemical Vapor Deposition (CVD) [2], Chemical Exfoliation (CE) [3] and Liquid Phase Exfoliation (LPE) [4] are the most promising for a potential large-scale production of graphene. Anyhow, also these approaches are not discharged from some drawbacks: for instance, the CVD, due to the high temperatures required for the synthesis of graphene, is an energy consuming method; in addition, the material needs to be transferred from the growth to final substrate, with a potential degradation of the film properties. The CE method through the chemical reduction of graphite oxide (GO) is commonly employed to synthesize graphene for industrial, large-scale applications thanks to the good solubility of the insulating GO in a common and simple solvent as water; as a counterweight, the reduction step, needed to obtain the conductive material (reduced-graphene oxide, R-GO), leaves many structural defects in the crystal lattice, decreases the water solubility and, additionally, generally employs highly dangerous chemicals, such as

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hydrazine. In comparison with the above described methods, LPE is a more sustainable process: it allows to produce graphene through the exfoliation of graphite in standard organic solvents [5–7] or simply hydro-alcoholic mixtures [8]. Furthermore, LPE-based graphene can be deposited by solution-processable techniques, like inkjet printing (IJP), a technology which allows to selectively deposit in a controlled manner minimizing the process steps and the waste materials.

In the present work, chemiresistive gas sensing devices have been fabricated by inkjet printing different LPE graphene suspensions on rigid and flexible substrates. The device performances have been investigated upon exposure to different concentrations of the gas NO_2 in environmental conditions.

2 Experimental

Different LPE graphene-based inks have been prepared. Starting from commercial graphite powder (Sigma-Aldrich, product 332461), a first ink (INK1) has been formulated by dispersing it in N-methyl-pirrolidone (NMP) (10 mg/mL) followed by a sonication for 3 h, and a second ink (INK2) by using a mixture of water/isopropanol (IPA/H_2O (1:7)) as solvent and sonicating the obtained dispersion for about 48 h. Then, each suspension has been centrifuged to remove the larger graphitic structures or the unexfoliated flakes and the surnatant has been taken as ink [9].

In order to analyze the surface morphology of the produced graphene, atomic force microscopy (AFM) measurements have been carried out in tapping mode by the Veeco Dimension Digital Instruments Nanoscope IV system. Moreover, the inkjet printed material has been also investigated by scanning electronic microscopy (SEM, LEO 1530).

Commercial alumina and glossy paper substrates with interdigitated gold electrodes have been employed as transducers.

The inkjet equipment was a Dimatix Materials Printer 2831 (DMP2831) of FUJIFILM—USA suitable for the print of functional inks onto flexible and rigid substrates. This system uses a piezoelectric drop-on-demand technology to eject droplets through a multi-nozzles printhead. The pattern of the printed sensing material was a rectangular surface. The chemi-resistor devices have been manufactured by printing a different number of graphene-based sensing layers, depending on the specific ink/substrate system. After printing, in order to remove the residual solvent a thermal treatment has been performed by keeping the devices on hot-plate at 100 °C for 15 min.

Tests for sensing measurements upon the analyte NO_2 have been performed in a stainless steel chamber placed in a thermostatic box, keeping constant the temperature ($T = 22$ °C), the relative humidity ($RH = 50\%$) and under a controlled environment at atmospheric pressure.

The sensing analysis has been carried out by biasing the single device at 1 V. Specifically, the measurement protocol has consisted of several sequential exposures at different analyte concentrations, where each exposure step has been preceded and followed by baseline and recovery phases, respectively, in inert atmosphere.

3 Results and Discussion

In our previous work [10], we demonstrated that IJP is able to deposit LPE graphene-based ink in a controlled manner so as to produce sensor devices with reproducible performances in terms of electrical response upon gas exposures. In that case, the ink was a dispersion of graphene in NMP and the employed substrate was alumina. Here we aim to further investigate the device-to-device variation as function of the number of printed layers and the base conductance. Therefore, by fixing the employed materials, chemiresistive sensor devices have been fabricated by inkjet printing the INK1 (see experimental section) onto gold/alumina transducers, and the sensing film has been obtained by printing a different number of overlapped layers (*n*). Just after their fabrication, the device have been electrically characterized in terms of initial resistance and sensing properties. The measurement results are summarized in Table 1. In detail, the initial resistance (*R*) has been detected in inert atmosphere under bias of 1 V, while the sensing properties have been analyzed through tests upon 10 min long exposure to the gas NO_2 and evaluating the conductance variation ($\Delta G/G_0$), namely the percentage variation of the conductance with respect to its initial value detected at the beginning of the exposure (G_0).

Table 1. Initial resistance (*R*) and conductance variation ($\Delta G/G_0$) values of the chemiresistive sensor devices fabricated by inkjet printing the INK1 (LPE graphene in NMP) onto gold/alumina transducers by varying the number of overlapped layers (*n*) to form the sensing film

Device	Printed layers	Initial resistance (kΩ)	Conductance variation (%) exp. to 1 ppm of NO_2
GR_NMP_IJP_2	2	400	3.5 (very noisy)
GR_NMP_IJP_3	3	10.2	2.5
GR_NMP_IJP_4	4	1.5	1.7
GR_NMP_IJP_5	5	0.6	1.5
GR_NMP_IJP_15	15	0.05	Unresponsive

As expected, by increasing the number of printed layers, and, hence, the deposited material, the devices become more conductive and the $\Delta G/G_0$ decreases. In Fig. 1, *R* and $\Delta G/G_0$ as function of *n* are reported. As it can be observed, both the parameters are well fitted by hyperbolic functions. This can be easily explained by assimilating the device as schematized in Fig. 2, where a section of the printed layer and the electrical contacts are displayed. Referring to that scheme, *R* follows the Ohm's law, $R = \rho * l/(w * t)$, where ρ is the resistivity. Assuming that each printed layer has always the same thickness (t_0) so that the final thickness of the sensing film is $t = n * t_0$, then *R* increases as *1/n* increases. Similarly, since $\Delta G/G_0$ depends on the specific surface (*S/V*, where $S = l * w$ is the exposed surface and $V = l * w * t$ is the volume), then also $\Delta G/G_0$ increases as *1/n* increases.

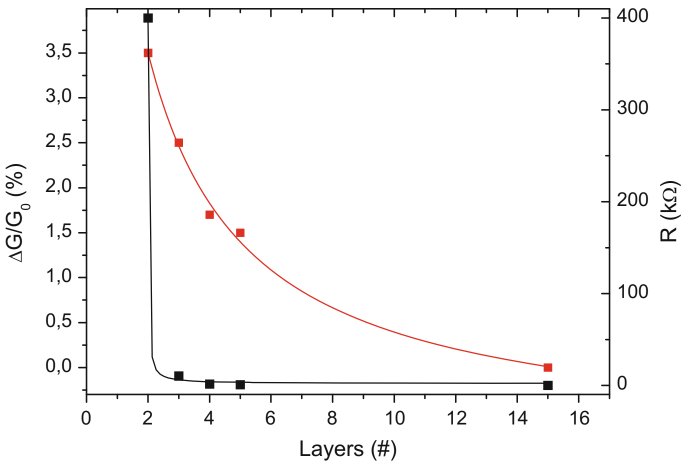

Fig. 1. Initial resistance (*R*) (*black*) and conductance variation (*ΔG/G₀*) (*red*) values versus the number of overlapped printed layers (*n*) and related fit curves (Color figure online)

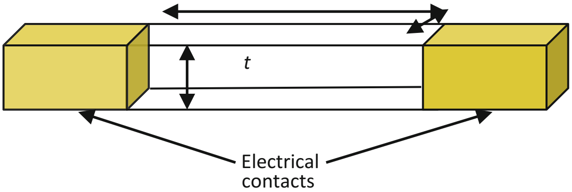

Fig. 2. Scheme of a section of the printed sensing layer and the electrical contacts of the manufactured chemiresistive device

Moreover, in order to investigate the possibility to fabricate graphene-based sensor devices by employing eco-friendly materials, the INK2 has been formulated by dispersing graphite flakes in a hydro-alcoholic mixture and printed onto glossy paper substrate.

The morphology of the printed material has been characterized by AFM analysis and the detected phase image is shown in Fig. 3. The AFM investigation shows a presence of restacked aggregates formed by planar-structured flakes. These structures are randomly distributed with cracks and gaps between neighbouring sheets.

SEM analysis confirmed this distribution of the printed material as AFM pointed out. By observing SEM image, displayed in Fig. 4, the deposition appears rather inhomogeneous and regions with overlapped flakes are clearly visible.

The material electrical property has been also investigated through the volt-amperometric characterization and the measurement results are reported in Fig. 5. The detected data I–V have been well interpolated by a linear fit showing the evident ohmic behavior of the material.

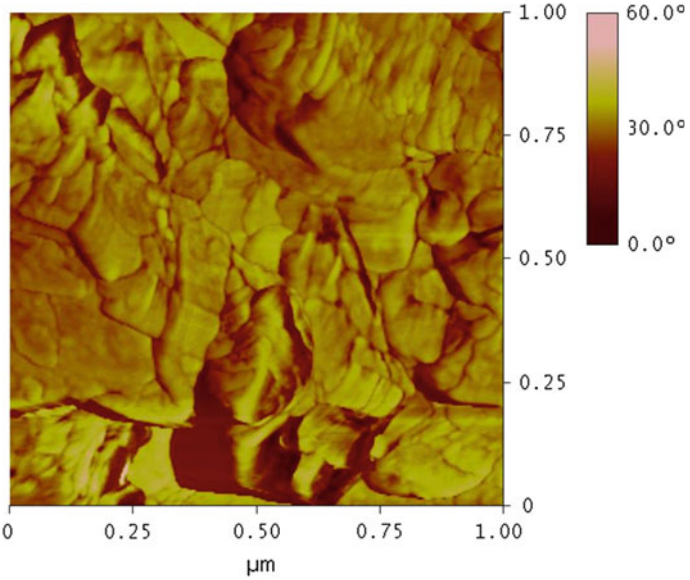

Fig. 3. AFM phase image of the sensing film printed by an aqueous graphene dispersion (scan size 1 × 1 µm^2)

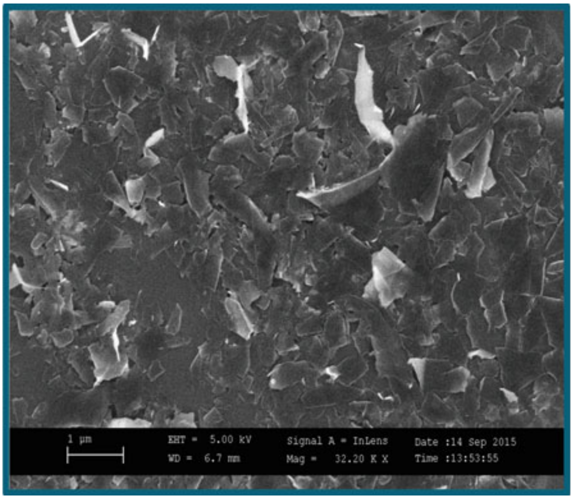

Fig. 4. SEM image of the printed graphene film

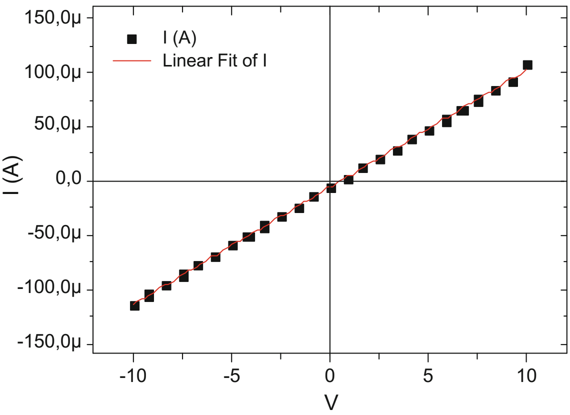

Fig. 5. I–V and related linear fit curve

The sensing property of the printed aqueous LPE-graphene chemiresistors has been tested by exposing them gas vapours of NO_2. Specifically, sequential cyclic exposures to the analyte at different concentrations have been performed, and the device outputs are reported in Fig. 6. As expected, during the exposure window to an acceptor analyte gas as NO_2, a conductance increase has been observed since LPE graphene is a p-type material [9]. It is worth noting that the device does not recover to the initial conductance value, so indicating that the material is not able to completely desorb the analyte. This also affects the sensitivity curve plotted by correlating the $\Delta G/G_0$ values to the NO_2 concentrations (Fig. 7).

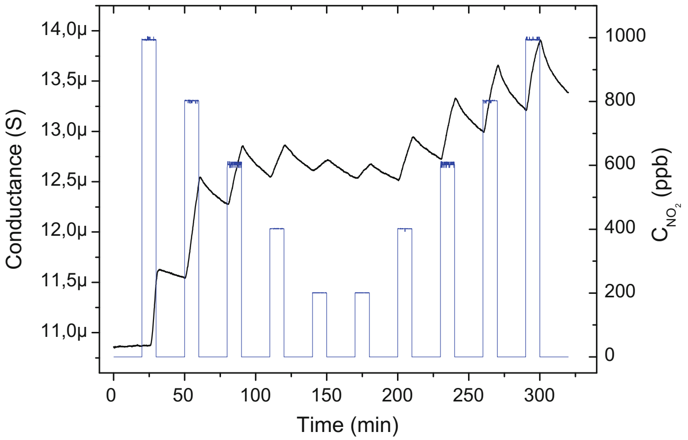

Fig. 6. Typical conductance behaviour of the chemiresistive device upon sequential analyte 10 min-long pulses (*dashed areas*) at different concentrations

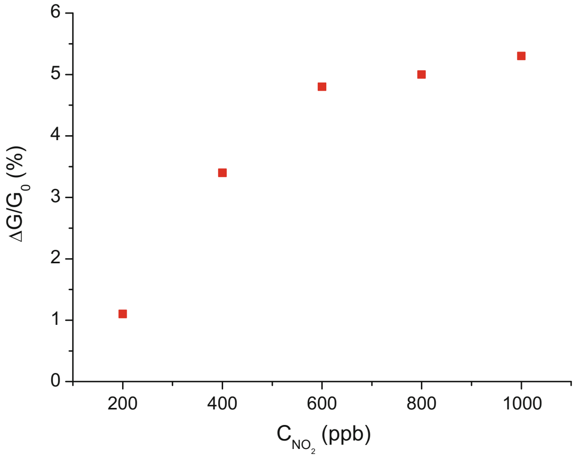

Fig. 7. Sensitivity curve: $\Delta G/G_0$ as function of NO_2 concentration

As it can be seen, at higher concentrations of the target analyte the curve diverges from a linear behavior, due to a poisoning effect of the sensing material. Nonetheless, good repeatability of the electrical responses upon identical exposures have been observed in the forward and backward cycles, as displayed in Table 2, where the $\Delta G/G_0$ values upon different concentrations of NO_2, ranging from 200 to 1000 ppb, are reported.

Table 2. Conductance variation ($\Delta G/G_0$) values of the chemiresistive sensor devices fabricated by inkjet printing the INK2 (LPE graphene in IPA/H_2O) onto gold/paper transducers upon different concentrations of NO_2 from 200 to 1000 ppb and vice versa

C_{NO_2} (ppb)	$\Delta G/G_0$ (%)	
	1000 ppb → 200 ppb	200 ppb → 1000 ppb
1000	6.8	5.3
800	8.5	5.0
600	4.6	4.8
400	2.5	3.4
200	0.8	1.1

4 Conclusion

In this work, we have manufactured chemiresistive gas sensing devices by inkjet printing different LPE (Liquid Phase Exfoliation) graphene suspensions, formulated in standard organic solvents (N-methyl-pirrolidone) or aqueous mixtures (water/isopropanol), on rigid (alumina) and flexible substrates (paper). The device performances have been investigated upon exposure to different concentrations of NO_2 and the device-to-device variation as function of the number of printed layers to form the sensing film and the base conductance has been investigated. By increasing the inkjet printed layers a higher conductivity has been obtained, and both the parameters of the initial resistance and $\Delta G/G_0$ decrease with a hyperbolic behaviour.

Furthermore, we demonstrated that the inkjet printing can be successfully adopted to fabricate graphene-based sensor devices by employing eco-friendly materials in order to address a sustainable approach in the processing chain, including functional (sensing) materials, substrates and technology.

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