

Enhancing the response to ammonia and nitrogen dioxide of bare graphene through NiPc functionalization

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Summary. — In this work, in order to enhance the sensing capability of bare graphene, nickel phthalocyanine (NiPc) powder has been sublimated through a thermal evaporator in ultra-high vacuum, and deposited as a monolayer on a graphene on silicon carbide substrate. After characterization, the functionalized sample and a bare graphene layer have been settled on a properly designed platform, able to monitor the sensor response of both chemiresistors, allowing for a direct comparison of their performances under the same working condition. The results clearly demonstrate that the NiPc functionalization improves the response of bare graphene to ammonia and nitrogen dioxide by 40% and 30%, respectively, at 10 ppm concentration.

1. – Introduction

Nowadays, gas sensors are quite essential in several fields, including environmental monitoring, food industry and transportation, breath analysis and security and public safety [1]. In particular, these sensors should be reliable, highly sensitive and selective, with fast response and recovery times; they should be low cost and with low power consumption and, preferably, they should work at room temperature, especially for wearable sensor applications [1, 2]. Among the materials exploited so far to develop gas sensors, metal oxides are certainly the most studied [3], but they present some drawbacks, including high-power consumption and high working temperature [4]. Therefore, researchers started to seek for new materials to be exploited as gas sensors, and in this framework, graphene is one of the alternative to metal oxides, due to its promising intrinsic properties, including ballistic transport, high surface sensitivity to gas molecules, low electrical noise and long term stability at room temperature [5, 6]. In addition to these remarkable electrical properties, bare graphene can be easily functionalized with different techniques and different molecules that can further improve its transport properties and consequently its sensing capability [7-9]. In this work, I will briefly report on our

attempt to functionalize bare graphene exploiting thermal evaporation in ultra-high vacuum of organic molecules, *i.e.*, nickel phthalocyanines (NiPc). In particular, NiPc have been selected due to their reported good sensing performances [10, 11], while thermal evaporation is a technique that offers good control on the layer formation and therefore allows for a high reproducibility of the sample. The sample functionalization has been performed at Elettra Sincrotrone in Trieste, as well as the electron spectroscopies (XPS, NEXAFS and ResPES) to characterize the functionalized sample, hereafter NiPc-Gr, which clearly show that a NiPc monolayer is horizontally flat deposited on the graphene layer and a charge transfer between the NiPc molecule and the graphene layer occurs due to a π - π interaction [12]. This charge transfer process influences and changes the electronic properties of bare graphene, opening up the possibility to enhance its sensing performances. After thorough characterization, a bare graphene layer and the NiPc-Gr sample have been settled on a platform, to simultaneously monitor their response to ammonia and nitrogen dioxide molecules in a chemiresistor configuration, disclosing an enhancement of the sensing response after functionalization. Finally, monitoring ammonia and nitrogen dioxide is important for several applications, including breath analysis and environmental monitoring. In detail, ammonia is the biomarker of liver and kidney failure [13] and it is the precursor of fine particulate, which is very dangerous for human respiratory health [14], whereas nitrogen dioxide is a potential biomarker of chronic obstructive pulmonary diseases [15] and it is one of the most common pollutants in atmosphere, which is very threatening for human beings [16], as it provokes damage to the environment, contributing to acid rain depositions, climate change, and tropospheric ozone formation [17].

2. – Materials, methods and characterization

Monolayer graphene on silicon carbide substrate has been purchased from GrapheneSic. Nickel phthalocyanine (NiPc) powder (Alfa Aesar, 98%) has been used as received. NiPc has been sublimated in UHV with a custom-made thermal evaporator and a deposition rate monitored by a homemade quartz oscillator (3 \AA in about 8 min). The functionalized sample will be labelled as NiPc-Gr. Raman spectroscopy (collected with a Renishaw-Invia system, equipped with a 633 nm laser source and a laser power of 5 mW), reveals the presence of the characteristic G-band (1590 cm^{-1}) and 2D-band (2660 cm^{-1}) of graphene [18] on the bare layer, as well as on the functionalized sample, while in the NiPc-Gr spectrum the presence of the NiPc peaks [11] confirms the effectiveness of the molecule deposition. AFM images, reported in ref. [12], show a homogeneous molecule layer formation for the NiPc-Gr sample. The electronic properties of the NiPc-Gr sample have been probed by X-ray photoelectron spectroscopy (XPS), near-edge X-ray absorption fine structure spectroscopy (NEXAFS), and Resonant photoemission spectroscopy (ResPES) at the N K-edge and Ni L_3 -edge. The results, discussed in [12], clearly show that a NiPc monolayer is horizontally flat deposited on the graphene layer, and that a coherent coupling between the NiPc layer and the Gr substrate occurs via π orbitals interactions, which leads to an electron transfer process. This experimental evidence is supported by DFT calculations; indeed, the analysis of the frontier molecular orbitals reveals the presence of some mixing between its molecular states and Gr. To carry out gas sensing measurements in a chemiresistor configuration, tracking the current (I) change of the sensing layers induced by the interaction with the gas molecules, electrical contacts made of silver paint have been printed as small stripes at the opposite sides of a bare sample and on the functionalized layer. Both samples, mounted on a properly designed

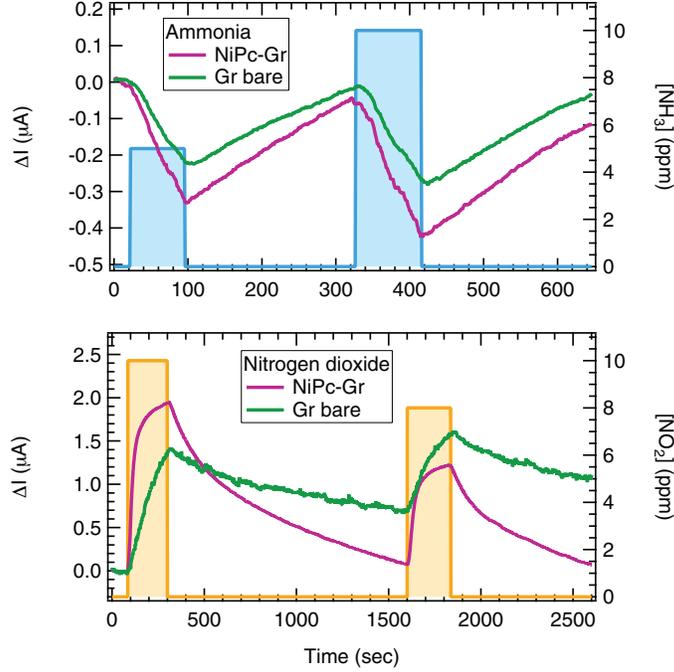


Fig. 1. – Current changes (ΔI) due to exposures to 5 ppm and 10 ppm of ammonia (top), and to 10 ppm and 8 ppm of nitrogen dioxide (bottom). Gas concentration can be read on the right axis, while current change is referred to the left axis.

platform, work simultaneously, allowing the direct comparison of the behaviour of the sensors under the same environmental conditions. Gas exposures have been carried out at room temperature in a sealed custom-made chamber, by introducing the analyte under investigation, *i.e.*, ammonia or nitrogen dioxide, through mass flow controllers (MKS Instruments). Two cylinders (certified by SIAD S. p. A.) have been loaded with 48 ppm of ammonia in synthetic air or 10 ppm of nitrogen dioxide in synthetic air, while a third cylinder has been loaded with synthetic air alone (SIAD Spa) and it has been used to dilute the concentration of the target gas in the chamber, as well as to purge the chamber after the exposures. The flow rate and exposure time for the gas interaction have been set so that the chamber was completely filled with the selected gas concentration. The same flow rate has been used also to purge the chamber, while the flow of synthetic air has been stopped as soon as at least one of the prepared sensors reached complete recovery. The response of the sensor is then defined as $\Delta I/I_0 = (I - I_0)/I_0$, where I_0 is the baseline sensor current before the gas exposure, and $\Delta I = I - I_0$ is the current variation due to the interaction with the gas molecules.

3. – Results and discussion

Figure 1 shows the preliminary results obtained for the bare graphene (green curve) and NiPc-Gr (light purple curve) sensors exposed to two concentrations of ammonia (upper side) and nitrogen dioxide (lower side), in terms of current change (ΔI). First, it is possible to notice that ammonia exposures leads to current decrease, while current

increase is observed during exposures to nitrogen dioxide. This result is in agreement with the reducing and oxidizing nature of ammonia and nitrogen dioxide, respectively, and to the p-type doped nature of both sensors. Secondly, it is possible to notice that the NiPc functionalization effectively improved the sensing performances of bare graphene. Indeed, the current change is higher for NiPc-Gr sample compared to bare Gr. In detail, the $\Delta I/I_0$ response enhancement thanks to NiPc functionalization is around 40% or 30% for 10 ppm of ammonia or 10 ppm of nitrogen dioxide exposures, respectively. Additionally, although a lower enhancement for the response, in the case of nitrogen dioxide, the recovery time is clearly improved in the functionalized sample compared to bare graphene. The improvement of the sensing response of the NiPc-Gr sample compared to the bare layer probably occurs in a twofold manner, *i.e.*, the different doping level of the functionalized layer due to the electron transfer process at the interface [12], and the probable catalytic role of the NiPc molecules themselves towards ammonia and nitrogen dioxide molecules. The present work represents a proof of concept on the feasibility to exploit phthalocyanine molecules to functionalize graphene layer and improve the sensing performances of bare graphene; of course, further investigation on the sensing mechanism, with particular attention also to the nature of the analyte, on the differences on the recovery time and on the selectivity of the presented sensors are required, additionally to exposures performed in a low-ppm range, which is the range useful for application in environmental monitoring, food quality tracking or breathomics, and stability tests. In particular, regarding stability, sensors based on graphene functionalized with phthalocyanine are expected to be stable at least over few months [19].

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REFERENCES

- [1] PARK S. Y. *et al.*, *Infomat*, **1** (2019) 289.
- [2] YUAN A. Z. *et al.*, *Sensors*, **19** (2019) 1495.
- [3] DEY A. *et al.*, *Mater. Sci. Eng. B*, **229** (2018) 206.
- [4] CHIU S. W. *et al.*, *Sensors*, **13** (2013) 14214.
- [5] VARGHESE S. S. *et al.*, *Sens. Actuators B*, **218** (2015) 160.
- [6] BOGUE R. *et al.*, *Sens. Rev.*, **34** (2014) 1.
- [7] NANDANAPALLI K. R. *et al.*, *Carbon*, **152** (2019) 954.
- [8] ALZATE-CARVAJAL N. *et al.*, *ACS Omega*, **5** (2020) 21320.
- [9] FREDDI S. *et al.*, *Angew. Chem. Int. Ed.*, **61** (2022) e202200115.
- [10] HO K. C. *et al.*, *Sens. Actuators B*, **77** (2001) 253.
- [11] FREDDI S. *et al.*, *RSC Adv.*, **12** (2023) 251.
- [12] CASOTTO A. *et al.*, *Nanoscale*, **14** (2022) 13166.
- [13] CHUANG M. Y. *et al.*, *ACS Sens.*, **2** (2017) 1788.
- [14] KIRKBY J. *et al.*, *Nature*, **476** (2011) 429.
- [15] FREDDI S. *et al.*, *Adv. Healthc. Mater.*, **9** (2020) 2000377.
- [16] OHYAMA M. *et al.*, *Health Res.*, **29** (2019) 632.
- [17] LAMMEL G. *et al.*, *Environ. Sci. Pollut. Res.*, **2** (1995) 40.
- [18] FERRARI A. C. *et al.*, *Nat Nanotechnol.*, **8** (2013) 235.
- [19] GUO Z. J. *et al.*, *RSC Adv.*, **9** (2019) 37518.