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Graphene functionalization for gas sensing applications

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Summary. — 2D materials show unique physical and chemical properties which can be exploited in several applications, including chemical gas sensors. Among the 2D materials, graphene has attracted particular interest, especially as a sensing element to detect and monitor concentration of different gases. Nevertheless, pristine graphene does not show remarkable performances as a gas sensor, and functionalization is often required to improve its sensing capability.

1. – Introduction

Although researchers have focused their effort on the development of gas sensors for many years now, thanks to their widespread applications, gas sensors are still attracting vast interest in the scientific community. Indeed, they have become quite essential in many fields: from the environmental monitoring and worker safety applications [1], which historically were the first applications of gas sensors, to medical care [2], which is probably the more recent application, passing through food quality tracking [3], industry processes and transportation. For all those applications, the sensor should fulfil some requirements: low cost, low energy consumption, quick response, fast recovery, and high sensitivity to low ppm concentration [4]. Furthermore, gas sensors could play an important role in the Internet of Things (IoT) field, not only from the perspective of smart cities, industries or homes, but also in wearable health monitoring devices, which have recently attracted considerable interest both in the research community and the sensor market. In general, among the challenges that the development of wearable gas sensors is facing, and in addition to the actual requirements for generic gas sensor applications, it is possible to mention that sensors need to be small-sized, flexible and comfortable to be worn, they need to be nontoxic, operate at room temperature and be able to monitor low target gas concentration among interfering gases. In the past decades, metal oxides have been the most exploited materials for gas sensing, but they present some limits, including high power consumption and high operating temperature, which make them not so good candidates to be exploited for the IoT wearable devices. Therefore, researchers have started to look into new suitable materials to develop gas sensors, with the aim to lower the detection limits, improve sensitivity, and develop small reliable devices. In this scenario, graphene is probably one of the most studied materials in recent

years, due to its intrinsic remarkable properties, such as its high plane conductivity and low electrical noise, its good chemical stability at room temperature, and its high sensitivity to surface adsorption of gas molecules, which make it a promising candidate for gas sensor development [5]. Within the graphene family, so far, graphene oxide (GO) or reduced graphene oxide (rGO) have been the most investigated for the development of gas sensors, since their highly defective nature is expected to favour the interaction with gas molecules, enhancing the sensor response. Nevertheless, GO- and rGO-based gas sensors have some drawbacks, from high production costs to poor recovery, to the initial condition after gas exposure, which makes their sensing capability unreliable [6]. Consequently, ad-hoc functionalization of pristine graphene has been recently explored as a methodology to enhance its sensing capability. Graphene could be functionalized in several ways, including both covalent and non-covalent bonding, and different experimental approaches could be followed for functionalization: from single atoms (mostly boron or nitrogen) to nanoparticles, or organic molecules. Here I will briefly report our attempt to exploit chemical covalent modification of graphene to develop reliable, stable and highly sensitive chemiresistor sensors for ammonia detection; in detail, following a protocol tested with high efficiency on highly oriented pyrolytic graphene (HOPG) [7], we prepared 3 functionalized samples and, after thorough characterization by AFM and Raman measurements, one pristine (Gr-pristine) and the 3 functionalized graphene layers were settled on a platform, to simultaneously monitor their response as chemiresistive sensors to ammonia molecules. This allowed us to directly compare the performances of the 4 sensors under the same working conditions. Ammonia monitoring is quite mandatory in several fields, from environmental monitoring to breathomics and food quality tracking. Indeed, ammonia is considered as the biomarker of liver and kidney failure, and, whereas in the exhaled breath of healthy subjects unconverted ammonia can be found in a concentration around 10 ppb, in the exhaled breath of subjects experiencing liver or kidney malfunctioning this concentration could rise up to 1 ppm [8]. Regarding environmental monitoring, ammonia is the precursor of fine particulate (PM2, 5 and PM10), which is very dangerous for human respiratory health and in general the concentration of ammonia in big cities (for instance Milan) settles down around 50 ppb [9]. Finally, spoiled food could release small quantities of ammonia (order of magnitude low ppm-ppb) [3]. Taking into account this information, it is clear why developing cheap and effective gas sensors to detect very low ammonia concentrations would be of great importance in many fields.

2. – Materials, methods and characterization

Monolayer graphene on silicon nitride substrates have been purchased from Graphenea. Powder of the diazonium salt precursors (Sigma Aldrich, 97%), as well as L-ascorbic acid (Sigma Aldrich, 99%) have been used as received. The covalent grafting procedure exploited to prepare the samples has been carried out by drop casting the ascorbic acid (20 mM) and the aryl diazonium salt precursor in a sequential way on a graphene sample. The reaction has been stopped after 20 minutes by rinsing the samples using acetonitrile and water followed by drying under an argon stream. Three samples have been prepared using diazonium salt precursors with different functional group at the top of the benzene ring: –COOH (Gr-CBD), –Br (Gr-BBD), and $–NO_2$ (Gr-NBD). Further information on the sample preparation can be found in ref. [7]. Raman spectroscopy (collected on a CGS device with a Renishaw-Invia system, equipped with a 633 nm laser source and a laser power of 2.5 mW), reveals the presence of the characteristic G-band ($1590\,cm^{-1}$)

and 2D-band ($2650\,\mathrm{cm}^{-1}$) of graphene [10] on the pristine layer as well as on the functionalized samples, while a strong increase of the D-band ($1340\,\mathrm{cm}^{-1}$) is evident going from the Gr-pristine to the functionalized layers. Consequently, the I_D/I_G value, which according to literature is used to quantify the degree of grafting [7, 10] dramatically increases in the functionalized layer, proving the effectiveness of the grafting procedure. In particular, the Gr-CBD sample shows the highest average I_D/I_G ratio, closely followed by the Gr-NBD sample and finally by the Gr-BBD layer. AFM images (acquired with a Park NX 10 AFM system in tapping mode at air-solid interface with a tip operating at a resonance frequency of about 160 kHz) shows an homogeneous molecule layer formation for the functionalized samples, with thickness of around 1 nm. To carry out gas sensing measurements in a chemiresistor configuration, tracking the resistance 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 pristine sample and on the functionalized layers. All samples, mounted on a properly designed platform, work simultaneously, allowing a direct comparison of the behaviour of the sensors under the same environmental conditions. All the ammonia exposures have been carried out at room temperature and in laboratory air, with a relative humidity value of RH $= (50 \pm 7)\%$. The exposure time has been set at 1 minute and recovery has been achieved in air. The response of the sensor has then been defined as $\Delta R/R_0 = 100 * (R - R_0)/R_0$, where R_0 is the baseline sensor resistance before the gas exposure, and $\Delta R = R - R_0$ is the resistance variation due to the interaction with the gas molecules, while sensitivity of the sensors (S) is defined as the sensor response normalized by gas concentration. Sensitivity is a parameter often used to compare the performances of different sensors. Generally speaking, it is quite important to obtain high sensitivity especially at low ammonia concentration, in order to meet the requirements of specific applications.

3. – Results and discussion

Figure 1 shows a sensitivity example of the four graphene-based sensors exposed to 8.5 ppm of ammonia. First, it is possible to notice that functionalization effectively improved the sensitivity of graphene. Furthermore, recovery is clearly improved in the case of Gr-NBD sample compared to the pristine graphene layer. Table I reports sensitivity at different ammonia concentrations. The best improvement is observed for the lowest ammonia concentration tested, *i.e.*, 0.37 ppm. Indeed, in this case the sensitivity is 4 times better for the Gr-BBD sample and almost 6 times better for Gr-CBD and Gr-NBD samples, compared to the pristine graphene layer. Looking into literature, the highest sensitivities for graphene-based chemiresistor sensors up to date have been reported to

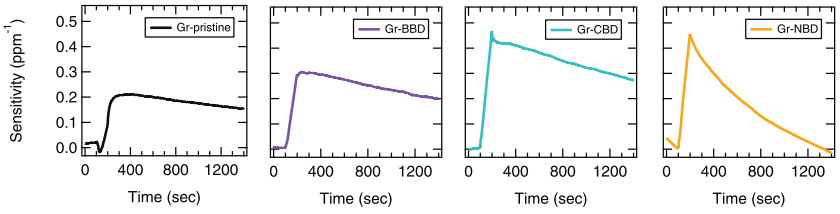

Fig. 1. – Sensitivity to 8.50 ppm of ammonia for the 4 graphene-based sensors. NH_3 exposure takes place from $t = 100$ s to $t = 160$ s. Gr-NBD and Gr-CBD show the highest sensitivity.

TABLE I. – *Sensitivity of the developed sensors at different ammonia concentrations.*

Concentration (ppm)	Gr-pristine (ppm^{-1})	Gr-BBD (ppm^{-1})	Gr-CBD (ppm^{-1})	Gr-NBD (ppm^{-1})
0.37	0.49	1.96	2.87	2.93
0.84	0.83	1.22	1.82	1.81
1.15	0.58	0.99	1.39	1.44
5.01	0.26	0.47	0.72	0.73
8.50	0.19	0.30	0.49	0.48

be 2.05 ppm^{-1} at 2 ppm [11] and 2.1 ppm^{-1} at 25 ppm [12]. Furthermore, no tests have been reported for concentrations lower than 1 ppm. Comparing this information with data reported in table I for the functionalized sensors, it is clear that the data obtained in the present work are quite remarkable in terms of sensitivity and, furthermore, the concentration limit has been pushed down and the presented sensors clearly responded in the sub-ppm ammonia range, where no literature results are still present. This is a very promising achievement, which opens the possibility to applications of these sensors in several fields, especially the ones for which sub-ppm concentration needs to be detected. The present work represents a proof of concept on the feasibility to exploit chemical grafting to functionalize graphene layer and improve the sensing capability of pristine graphene; of course, further investigation on the sensing mechanism and the selectivity of the presented sensors is required, as well as stability tests, nevertheless the sample procedure preparation and the responses to ammonia are quite promising.

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