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A route to detect H₂ in ambient conditions using a sensor based on reduced Graphene Oxide

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Abstract

Graphene Oxide (GO) is considered an ideal candidate for the fabrication of hydrogen gas (H₂ (g)) sensors due to its excellent capabilities for direct wiring, thanks to the presence of functional groups, which provide an opportunity to modify its chemical functionalities. In this study, we have fabricated a H₂ (g) sensor based on the precise positioning of GO flakes across sputtered aluminium-doped ZnO (AZO) electrodes on a glass substrate using a positive dielectrophoretic force (DEP). GO flakes assembly was performed between AZO electrodes gap of 4 μm and optimized by controlling the DEP parameters. A chemical reduction using a solution of 10 mM sodium borohydride was used to enhance the conductivity of the GO flakes up to two orders of magnitude. The arrangement of the GO flakes, the efficiency of the reduction process, the morphology and the surface potential of these was analyzed by Atomic Force and Kelvin Probe Microscopies. A reduced Graphene Oxide (rGO) work function in the range of 4.7-4.9 eV was obtained. Moreover, the H₂ (g) response of rGO/AZO sensor was studied by two types of tests. First test consists of a single 10 min exposure of pure H₂ (g), collecting the IV directly data in order to obtain the sensitivity of the rGO to be of ~100 % at 1 V. Second test consists of a batch of different time exposures to analyze the stress performance and the saturation level of the sensor. Finally, the impact of the ambient conditions on our sensor sensitivity was studied.

Keywords: Graphene Oxide, dielectrophoresis, hydrogen gas, and sensor.

1. Introduction

In order to be able to supply the energy needs of the world's population, the scientific community is constantly looking for new forms of energy produced in more efficient and clean ways than those currently employed. A considerable attention has been paid to produce hydrogen-based energy systems not only because H is the most abundant element in the universe, but also because it is considered a renewable energy source [1] [2][3]. The handicap is that H gas is invisible, odorless and is categorized as an element

highly flammable at concentrations higher than 4% in air. Therefore, it is mandatory to fabricate sensors that are able to detect possible leaks of hydrogen. In the last years, graphene has been considered as a remarkable candidate material for the detection of gases such as H_2 [4], CO_2 [1][5] and NO_2 [6][7] among others thanks to its large surface area, which enhances its sensing performance, and to the excellent capabilities of their sp^2 -bonded carbon atoms (lower binding energy required) for direct wiring with different molecules. Graphene is a 2D material consisting in a monolayer of carbon atoms with a sp^2 hybridization. This material is a zero-gap semiconductor that allows sensing the absorption/desorption of different molecules by means of the monitoring the changes in its electrical conductance [8]. In fact, Schedin et al. [9] demonstrated the detection of single gas molecule by a graphene based-sensor maximizing the signal-to-noise ratio to a level sufficient to detect variations in a local carrier concentration by less than one electron charge. The issue is that the mass synthesis of graphene still represents a technological challenge, not to mention its high cost.

The use of graphene oxide (GO) has attracted a lot of attention as an alternative to produce graphene in an easiest and cheapest way. GO is an inorganic material that possesses oxygen-containing groups [10] at its basal plane (such as epoxide C-O-C, hydroxyl C-O) and its edge (such as carboxyl O-C=O, and carbonyl C=O) that make it hydrophilic. This property allows to deposit it using simple contactless techniques such as drop casting [11], dip coating or dielectrophoresis, among others [12][13], on any sort of substrate. Although GO is an electrical insulator, it is well known that under the action of certain reducing agents, such as sodium borohydride ($NaBH_4$) or hydrazine, and also via thermal processes [10][11][14][15], the properties and structure of graphene can be partially restored. Among these, $NaBH_4$ has demonstrated to be very efficient [16], as well as to give the chance of working with flexible substrates, in contrast with thermal processes. Shin et al. [17] used $NaBH_4$ at different concentrations (15mM, 50 mM, 150 mM), showing a significant increase in the ratio of the C=C bonds, reducing C=O species, and almost removing all epoxy and carboxyl groups, restoring satisfactorily the graphene properties.

Among the available techniques for trapping GO, the dielectrophoresis (DEP) is a very suitable one. As a matter of fact, DEP can contribute to selectively align micro and nanoparticles between electrodes, with a thickness ranging from a single monolayer to several layers over a large area [18]. DEP force arises from the induced dipole moment $p(t)$ in a particle when it is placed in a non-uniform electric field $E(t)$. DEP force is defined by the expression $F_{DEP} = (p(t)\nabla)E(t)$ where the dipole moment and the electric field depend on time, and its strength is directly linked to the dielectric properties of both the particle and the

suspension medium, the amplitude, frequency and phase of the electric field. The origin of the DEP force is the non-compensated coulomb forces at both sides of the particle, due to the non-uniform electric field, what produces a change in the particle movement. Indeed, the DEP force has a translational character.

The aim of this work is to present a $H_2(g)$ sensor based on reduced GO (rGO), in which a precise positioning of graphene oxide flakes was done by dielectrophoresis. For that, we used sputtered aluminium-doped ZnO (AZO) electrodes on a glass substrate. The GO sheets assembled in this way were reduced by a chemical treatment ($NaBH_4$). The work function (ϕ) value of the rGO sheets assembled were studied by scanning Kelvin Probe Method (SKPM). The final performance of the $H_2(g)$ sensor was analyzed under two different conditions: a continuous 10 min exposure and a stress test with an increasing time exposure.

2. Experimental

The rGO-based sensor was fabricated using an AZO/GO/AZO configuration as displayed in Fig. 1a. The fabrication was checked at different stages by using an optical microscope and current-voltage (I-V) characteristics. First, an aluminum zinc oxide (AZO) film with a thickness of 200 nm was deposited on a glass substrate by RF sputtering system in pure Ar ambient with a power of 150 W and an Ar flux of 50 sccm (working pressure of 10^{-2} mbar). The election of AZO was due to its good conductivity, stability, and sticking properties on many different substrates, including flexible ones. Afterwards, two elongated electrodes were fabricated using the AZO film by a combination of photolithography and chemical wet etching ($H_3PO_4 + CH_3COOH + H_2O$ (1:1:75)). The electrode width was 100 μm with a separation between them of $\sim 4 \mu m$. Aluminum contact pads with a thickness of 500 nm were sputtered later on each AZO electrode.

Dispersed GO flakes in an aqueous solution were purchased from Graphenea. The flakes had dimensions ranging from ~ 6 to 32 μm in size and a concentration of 4 mg/mL. Achieving a good control of the assembling parameters of the flakes in a specific area is required in order to obtain a homogenous and smooth deposition of them. For that aim, a home-made microfluidic DEP system was used (see Fig. 1b) [19].

The procedure followed to attain the assembly of GO flakes between the AZO electrodes *via* DEP begins with the further dilution of the GO solution in water up to concentration 5 $\mu g/mL$. This density was chosen to obtain a higher percentage of monolayer flakes and therefore to avoid the formation of agglomerates of

the GO flakes i.e., to achieve very thin sheets. The inlet tank was filled with this solution and pumped into the area between the electrodes, where a non-uniform electric field was applied with a constant flow rate.

The characteristics of electric field (frequency, voltage amplitude, and processing time) were chosen to create a positive DEP force, which produces the trapping of GO flakes in the interelectrode region, where the electric field is maximum. GO was selectively aligned under different DEP parameters in order to optimize the experimental conditions. An AC signal with a 500 kHz frequency was applied between electrodes under three different peak-to-peak voltages (V_{pp}): 10, 15, and 20 V. The duration of the each process was 1 min. The resulting I-V curves obtained after the DEP processes showed that the experimental runs carried out at a V_{pp} of 10 V and 15 V presented a very poor signal-to-noise ratio (Fig. 2). For the sake of comparison between the performance of the device under forward and reverse biases, note that Fig. 2 shows the absolute value of the current. However, that made at a V_{pp} of 20 V showed a high signal-to-noise ratio, and an ohmic behavior indicating a well aligned current path between AZO electrodes, therefore a good assembly of the GO flakes. Thus, the rest of the devices reported here were fabricated at a 500 kHz frequency, a V_{pp} of 20 V, and a processing time of 1 min.

After DEP, the device was blow-dried with nitrogen. Typically, the sensor's sensitivity to gas exposure is measured by the changes in this resistance. However, we have observed that our sensor with as-deposited GO showed no response to an exposure of 40 sccm of pure $H_2(g)$. An efficient method to enhance the sensing properties of our sensor involves the removal of the oxygen-containing groups and defects contained in GO to create more unsaturated carbon atoms (graphitic domains), and consequently producing more reactive sites for gas adsorption and making easier the current transport. It is well known that this aim can be reached by using certain reduction techniques which may remove those groups, and restore somehow the graphene structure. Following this route, GO assembled between the electrodes (hereinafter "rGO/AZO") was reduced by a 10 mM $NaBH_4$ solution in atmosphere during 4h. Immediately after rGO/AZO was electrically characterized in a probe station.

In order to study the effect of the reduction process, the morphology and the surface potential of the rGO flakes was analyzed by scanning Kelvin probe method (SKPM) using an Agilent PicoPlus 5500 system, operating in dynamic mode. For these measurements, platinum-coated cantilevers with a nominal force constant of $3.5 \text{ N}\cdot\text{m}^{-1}$ and radius of 20 nm ($\text{C}\mu\text{masch}$) were employed. Kelvin probe force microscopy (KPFM) measures the contact potential difference, which is the difference in the work function values of

the imaged sample location and that of the tip. Images were analyzed and post-processed with Gwyddion program [20]. Besides, micro-Raman measurements were performed before and after reduction procedure, with a custom made system using the 488 nm emission of an Ar⁺ laser, an Olympus microscope with a 100x objective, a notch filter and a monochromator and CCD camera from Horiba.

The sensing test was carried out in a high-vacuum chamber with a fixed gas controlled with mass flow controller (MKS 100). Two types of tests were performed, both using a top-down hydrogen flux 40 sccm at 10^{-7} mbar. First test consists of a single 10 min exposure, collecting the I-V directly data after that. Second test consists of a batch of different time exposures to analyze the stress performance and the saturation level of the sensor. This test was simultaneously done in both the sensor and a reference sample described later on. All the electrical measurements were done in a probe station at RT and ambient conditions collecting the data with a 4145B Packard Bell parameter analyzer in DC mode. Finally, in order to check the impact of the water vapor and to focus on only the contribution to the conductivity from rGO flakes aligned between the electrodes, a new sample was fabricated following the same steps and conditions as rGO/AZO had. Nonetheless, the electrodes were only fabricated with Aluminum instead of AZO (hereinafter “rGO/Al”). To carry out this analysis, the rGO/Al sensor was introduced into a climatic chamber (Mettler HCP108), and subjected to 60% relative humidity at 30 °C for 1 hour.

3. Results and discussion

First characterization of the rGO/AZO was done by KP-AFM (Fig. 3), which can give an estimation of the work function of the flakes after the reduction process. Fig. 3a shows a sketch of the device and the analyzed area by KP-AFM. From Fig. 3b, one can see that film surface formed by rGO flakes is homogenous, demonstrating the success of the DEP process, and the good alignment of the flakes with the electrodes. Hereinafter, we will focus on the region selected in Fig. 3b by a dashed white line (labelled as Area I). Note that Fig. 3d shows a zoom of Area I. The cross-sectional height profile (Fig. 3c) shows the thickness of rGO film was ~ 4 nm, and remains essentially constant over the whole contact area (Fig. 3c). The contact surface potential was used in order to estimate the WF of our reduced GO. The average of the contact surface potential difference within the Area I was assessed to be 1.42 ± 0.15 V (see Fig. 3b, 3d and 3e). By looking in more detail inside this area, two flakes (labelled as F1 and F2 in tapping-mode AFM Fig. 3d) with different dimensions were chosen as representatives of the structure. Sizes were approximately ~ 1 μ m and 4 μ m for F1 and F2, respectively. The contact surface potential difference for F2 (1.56 V) shows a value

slightly higher than that found for F1 (1.40 V), which indicate in principle that larger flakes show a lower work function (ϕ). In fact, Sygellou *et al.* [21] studied the effect of the flake size in the rGO work function tuning, demonstrating that larger flakes showed a lower ϕ values than the smaller ones, which is in good agreement with our results. Furthermore, they also studied the variation of rGO work function value with the use of different reduction agents; finding that this variation, which can be as high as 1 eV between GO and highly rGO, is not only due to the concentration of oxygen functional groups but also to the thickness of the rGO layer. The low value found for ϕ in both cases is ascribed to the low concentration of the C=O groups, since NaBH₄ is very effective removing these groups [21]. Despite the difficulty for obtaining accurate quantitative surface potential for KFM measurements under ambient conditions [22], the rGO work function in Area I (average value), F1 and F2 can be indirectly estimated from the Contact Potential Difference (V_{CPD}) values measured at the different surface features in Fig. 3b, and using the AZO contact potential as a reference material ($\phi_{AZO}=4.62$ eV) [23]. We applied the rule $V_{CPD} = \frac{\phi_{tip} - \phi_{sample}}{e}$, where V_{CPD} is the contact potential different, ϕ_{tip} is tip work function, ϕ_{sample} is the work function of rGO or AZO accordingly, and e is electron charge in order to obtain an estimation of the rGO work function in Area I, F1 and F2. Thus, the voltage values obtained for the flakes can be converted to ~ 4.71 , 4.86 and 4.70 eV for Area I, F1 and F2, respectively. For comparison, an epitaxial monolayer graphene on SiC has a $\phi \sim 4.30$ eV, saturating at 4.60 eV for more than 10 graphene layers [24]. This saturation value is not too far from our ϕ estimations for a ~ 4 nm rGO film (Area I), wherein more than 10 graphene layers are contained, indicating the proper reduction. As a comparison, Misra *et al.* [25] found that the work function of the rGO gate electrode in a metal oxide semiconductor transistor (CMOS) can be tuned from 4.35 to 5.28 eV by changing the rGO thickness. Thus, our value for ϕ is compatible with these findings. Figure 4 presents the Raman spectra of the as received GO and that obtained after the reduction process with NaBH₄. The intensity ratio between G and D peaks is commonly used as an indication of the defect content in graphene. D peak is related to the presence of defects, then, the less defects the less intensity, so a decrease of ID/IG indicates less defects, which is true for moderately defective graphene. However, graphene oxide is a heavily defective system where a large fraction of the C rings has lost the aromatic character through bonding to oxygen functional groups (CO, COOH and OH, typically) and a large fraction of C sp³ in present in GO. Since D band requires defects but also requires aromatic rings, in the first reduction step an increase of ID/IG is observed due to the restoration of aromatic rings density by elimination of functional groups. Further reduction decreases the defects concentration and then ID/IG drops. While the ID/IG ratio presents

a non-monotonous behavior upon reduction (first an increase and then a decrease), it is useful to rely on the widths of the D and G peaks that show a constant decrease upon reduction [26]. In the present case ID/IG increases up to 1, which corresponds to the inflection point of this ratio, and the widths of the peaks decrease indicating unambiguously that graphene oxide has been partially reduced.

The electrical characterization of the rGO/AZO sample at all states is shown in Fig. 5. I-V curve after DEP process shows a symmetrical behavior of the I-V curve, indicating the well alignment of the GO flakes, and analogous contact between the flakes and AZO in both electrodes. The resistance of rGO/AZO sensor was found to be 170 M Ω at 1 V, what means a decrease of two orders of magnitude in comparison with that before NaBH₄ at 1 V (15.5 G Ω). In order to check the response of rGO/AZO to H₂(g), the sensor was loaded in a vacuum chamber and exposed to a top-down hydrogen flux 40 sccm, at 10⁻⁷ mbar pressure, for 10 minutes at room temperature (RT). After the exposure was completed, the sensor response was immediately measured in the probe station in ambient conditions at 39.7% of relativity humidity (RH) (see Fig. 5a). Fig. 5b shows the change in the electrical resistance ($R = dV/dI$ versus V dependence) of the rGO/AZO immediately after H₂(g) exposure, observing that the conductance of rGO/AZO has increased due to the uptake of H₂(g). This phenomenon is due to the donor character of H impurities [11] [12] [2] [27], which supply electrons to the rGO sheets giving rise to the observed increase of the conductivity. Indeed, the exposure of our rGO/AZO to H₂(g) produces a measured resistance change of about 2 orders of magnitude (Fig. 5b). That means a sensitivity of the r-GO of ~100 % at 1 V, which is defined as $\frac{R-R_0}{R_0} \times 100$, where R is the resistance of the rGO/AZO exposed to H₂(g) and R_0 is at ambient conditions. This demonstrates the excellent performance of our rGO/AZO sensor.

The next characterization step consisted in subjecting the rGO/AZO sensor to the batch described in the experimental part. The resistance was measured immediately after exposing the sensor to H₂(g) for every sequential step. Note that the sensor was accumulating the time exposure to hydrogen flux. In addition, to dismiss a possible contribution of the AZO electrodes, a test sample (hereinafter “AZO”), with the same geometry as rGO/AZO, but without an electrode gap (no GO), was introduced into the vacuum chamber simultaneously to rGO/AZO. Fig. 6 shows the evolution of the resistance at 1 V of rGO/AZO sensor and AZO sample with time. As can be seen from figure, two regimes can be identified. The first one corresponds to the first 30 minutes of accumulated exposure to H₂(g), where the sensor seems to have reached the saturation state. In the second one, the resistance stays practically unaffected to H₂(g) exposure during more

than one hour and a half. Remarkably, the AZO sample did not show any sensitivity to the hydrogen flux over time, what rules out the effect of the electrodes in the process, confirming that the active layer of the gas sensor is the rGO. It is well known that sp^2 carbon atoms bond weakly with the $H_2(g)$ molecules [11]; on the contrary active oxygen functional groups and carbon atoms bond strongly, not only to $H_2(g)$ molecules, but also to H_2O molecules [28]. Thus, a potential reason for the slow response of our sensor could be the progressive replacement of H_2O molecules previously attached to rGO surface with $H_2(g)$ molecules.

The role of ambient humidity is therefore an important issue that can limit the response of our rGO/AZO. Tjoa et al. [7] paid attention to the role of water vapor in GO and they tested this hypothesis studying the unintentional doping effects of oxygen and H_2O vapor in a rGO-nanoparticle hybridization in a transistor configuration, detecting a drastic drop of the conductivity in the transistor resulting in p-type transport. Moreover, H. Ren et al. [29] recently studied the effect of the humidity on a NiO@rGO sensor (at 40, 58, 70 % humidity) at 50 °C, observing a slightly increase of the response as the humidity increases. Taking into account the importance of water vapor in rGO electrical properties [30], we decided to further study this effect too. As was mentioned in the experimental section, in order to focus on only the contribution to the conductivity from rGO flakes aligned between the electrodes, a new sample rGO/Al was used. Note that the electrodes were fabricated with Aluminium instead of AZO in order to prevent any unintentional contribution from AZO. The sample rGO/Al was introduced in a climate chamber (Mettler HCP108), and subjected to an extreme conditions (60% relative humidity at 30 °C for 1 hour). The impact of the vapor in the electric properties was estimated measuring the I-V characteristic immediately after the exposure (see Fig. 7). The figure shows that the resistance of the rGO/Al increases in such a way it returns to the same state before reduction process. This result reveals that water molecules could act as acceptors impurities, compensating somehow the existing shallow donors, and thus raising the resistance of the rGO. Therefore, it seems plausible that the $H_2(g)$ sensitivity of our rGO/AZO sensor could be improved under vacuum conditions. In fact, Wang et al. [11] measured sensitivities ranging from 300 to 600% for a concentration of hydrogen gas from 30 to 160 ppm, respectively for highly reduced GO loaded in a vacuum chamber in situ.

4. Conclusions

We have successfully developed a $H_2(g)$ sensor based on rGO and AZO electrodes. The electrical response of the reduced GO flakes was locally investigated by KPFM, obtaining a work function in the range of 4.7-

4.9 eV, in good agreement with previous works. This work function is consistent with the thickness found for the deposited flakes, which is in the range of 4 nm thick. The sensor was tested in a vacuum chamber and characterized ex-situ using two different approaches: single and batch modes. For the single H₂(g) (40 sccm, 10 min) exposure the sensor shows a decrease in the resistance from 100 to 1 MΩ. For the batch tests, we found out that the resistance reaches a stationary state after 30 min of sequential exposure, what is interpreted as a complete saturation of the free bonds in the rGO flakes. Finally, we have shown that relative humidity is a critical factor for the performance of these devices, what suggests the need of more controlled in-situ experiments for a proper calibration of these devices.

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Figure Captions

Fig.1 **a** rGO-based sensor using an AZO/GO/AZO configuration and microscope view zoom of rGO between AZO electrodes, **b** Sketch of the home-made microfluidic DEP system

Fig.2 Current-voltage characteristics of the GO flakes deposited in the interelectrode region at peak-to-peak voltages of 10 V, 15 V and 20 V. Same frequency (500 KHz) and deposition time (1 min) were used in all the cases

Fig.3 **a** Sketch of the device and into black dotted square the analyzed area by KP-AFM. **b** Tapping-mode AFM of rGO device assembled via DEP. At the bottom and top edges of the photo, a pair of AZO electrodes with a gap smaller than 6 μm is observed. **c** Height profile of the rGO flakes and glass at different positions. **d** zoom-in view of the rGO flakes F2 and F1 framed with white dashed lines. **e** Contact surface potential difference using a scanning Kelvin probe method (SKPM) measured simultaneously

Fig. 4 Raman spectra of GO and chemically reduced GO (10 mM NaBH_4)

Fig.5 **a** Current-voltage characteristics of rGO/AZO before DEP, after DEP, NaBH_4 reduction, and $\text{H}_2(\text{g})$ exposition (40 sccm, and 10 min). **b** Measure of resistance of rGO/AZO after reduction and immediately after $\text{H}_2(\text{g})$ exposition (40 sccm and 10 min)

Fig.6 Change in resistance of rGO/AZO and AZO sensor under an accumulated exposition at 40 sccm of $\text{H}_2(\text{g})$ over time

Fig.7 Impact of the water vapor in the current-voltage characteristics before reduction, after, and after exposition at 60 % RH.

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