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Graphene oxide/Cu junction as relative humidity sensor

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Abstract

The paper investigates the electrical properties of the junction between the graphene oxide (GO) and some metals (Cu and Au). A simple humidity sensor, based on the adsorption of water molecules on the GO/surface in a GO/Cu junction, is described. The GO was drop-casted as a thin film, 10 µm in thickness, on the metallic substrate. The junction open-circuit voltage and short-circuit current behaviours versus the humidity level can be explained on the base of the charge carrier drift. The room temperature response of the GO/Cu water vapour detector, in terms of relative humidity in air, is compared against a well-known commercial hygrometer. The proposed device does not require external polarization, and it is inexpensive and easy to use.

1 Introduction

Graphene oxide (GO) is a 2D special material derived from the graphite exfoliation, which consists in micrometric and sub-micrometric platelets with nm thickness and different chemically bonded functional oxygen groups [1, 2]. In fact, GO is rich in small sp^2 carbon clusters, while sp^3-hybridized bonds occur with oxygen on the basal plane and at the platelet edges giving GO hydrophilicity and sensitivity to water molecules [3, 4].

GO is a good insulator from the point of view of the electrical properties, but its chemical or physical reduction, eliminating the functional oxygen groups, transforms the sheets in good conductive ones, changing their electrical conductivity of about 6–8 magnitude orders, depending on the reduction level [5, 6].

GO has high absorbance in the UV region and relatively low absorbance in the visible region. Its transmission in the IR region is high except at specific wavelength absorption bands due to the carbon bonding with some functional groups, such as the –OH ones [5]. GO has excellent mechanical properties such as high flexibility, tensile strength, Young module and rupture load. It has low thermal conductivity which is modified in the presence of reduction [3].

GO films possess a nanoporosity, through which they become permeable to many atomic and molecular species, to some gases and liquids. Particularly, they are highly permeable to water, which, driven by capillary forces, is confined between the GO nanometric channels. GO more easily uptakes water molecules from the vapour phase than in liquid phase unlike graphite [4]. GO also absorbs very well H_2, Li, O_2, N_2, CO and CO_2 [7].

These properties permit to develop many GO-based devices in ambit of electrical, thermal, optical, mechanical and chemical sensors [8, 9]. For example, using a GO-silicon bi-layer flexible structure, stress-based humidity sensors have been realized. This type of sensors shows fast response and recovery times, a little hysteresis, but needs a high working voltage (5 V), which results in high power consumption [10].

Reduced graphene oxide (rGO) can be obtained thermally, chemically, by impact of energetic particles or photons [11–13]. The removing of many oxygen functional groups confers to the material new properties: high electrical and thermal conductivity, high transmittance in the IR region, high mechanical resistance and others similar to those of graphene.

In recent years, attention has also been paid to the graphene–metal interface. In particular, a theoretical and experimental study of graphene–metal contacts has highlighted

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about the nature of the graphene–metal interface at the most fundamental level. By using different graphene–metal contacts, it has been possible to develop a simple analytical model of the graphene–metal contact based on few parameters and to devise ways of experimental validation [14].

Also the GO–metal and the rGO–semiconductor junctions allow to realize new electronic devices: light sensors, diodes, transistors,… [15]. The junction energy barrier can be controlled via the GO reduction level and allows the charge separation and collection through an applied electrical field [16]. Therefore, based in turn on GO, GO–metal or rGO–semiconductor junctions, it is possible to develop useful thermal sensors, ionizing radiation detectors, films with optical properties adapt to be employed in solar energy conversion, membrane to purify water, gas and humidity sensors [8, 17–19].

The properties of GO depend on the content of its functional groups (carboxyl, epoxy, phenol, carbonyl and others) that allow fast water permeation within the GO layers and a rapid water molecule diffusion during humidity changes [20]. In fact, the literature reports that water molecules adsorbed at the GO surface modify the GO electrical conduction depending on the humidity degree. Usually GO shows a p-type semiconductor behaviour with the carrier concentration dependent upon the degree of oxidation [21]. This behaviour is due to the presence of C–O bonds in which the O atom tends to pull electrons from the C atom, leaving a hole in the carbon network. Since H_2O is an excellent electron donor, it decreases the GO holes density enriching the electron concentration and leading to a decrease in its conductivity [22, 23]. In this way, in GO electronic and ionic conduction mechanisms are present and the prevalence of one over the other depends on the degree of humidity. In the absence of humidity, i.e. dry air, the electronic conduction is basically dominated by the concentration of surface charge carriers on GO, which is usually hole concentration. At low humidity (about 6–20% relative humidity, RH), the water molecules, chemisorbed on the GO surface, dissociate according to the following reaction: $H_2O \leftrightarrow H^+ + OH^-$to form surface hydroxyls. After the hydroxyl formation, the next water molecules will be physisorbed via hydrogen double bonds on the two neighbouring hydroxyl groups and a proton may be transferred from a hydroxyl group to water molecules to form a hydronium (H_3O^+) ion. At this stage, the concentration of hydronium ions is very low due to the high ionization activation energy [23]. Since the new formed H_3O^+ ion releases a proton to a nearby water molecule ionizing it and forming another H_3O^+ group, a proton hopping mechanism occurs from one water molecule to another (the so-called Grotthus chain reactions [24]). At medium humidity (about 20–65% RH), the physisorbed water molecules can form a continuous layer on the GO surface and can also possibly permeate within the GO layers giving rise to a GO swelling and increasing the concentration of hydronium ions and consequently the ionic conductivity. With a further increase in RH (at high humidity, about 65–95% RH), multilayers of physisorbed water molecules on the surface as well as between the GO layers are highly probable and the hydrolysis of various oxygen-containing functional groups can take place yielding a high amount of ions H_3O^+ and increasing the ionic conductivity: the dominant charge carrier becomes the H^+ (proton) [22, 23].

In the insulating GO, the electrical conduction can be due to transport of electrons and/or holes and their trapping and de-trapping (tunnelling) occurring at room temperature. This is due to the embedded graphene inclusions that are thought to be capable of capturing charge carriers. In particular, in test structures of Au/SiO_2/GO/SiO_2/Si two groups of traps capable of capturing both electrons and holes in GO were detected by means of the charge deep-level transient spectroscopy (Q-DLTS). These levels seem to be inherent to graphene islands, with and without p-doping with oxygen. In them charge carriers are emitted from energy levels in the vicinity of the Dirac point [25].

In light of the above, to our knowledge, no information is reported in the literature about detailed studies on the GO/Cu junctions that could have interesting practical implications in the field of sensors.

This paper reports the results about the detection of the relative humidity in air using a GO/Cu junction-based sensor. They are presented subdivided in three parts. The first part is dedicated to measurements on the investigated electrical properties of the GO/metal junction. The second part presents the response of a GO/Cu junction to water vapour signals. The third part proposes a new calibrated GO/Cu junction hygrometer. This last is based on the measurement of its open-circuit voltage or short-circuit current and shows high sensitivity, good reproducibility and reliability. The device operates at room temperature and does not require an external bias. It can be integrated into smart humidity monitoring systems to measure the humidity levels on a specific environment.

2 Experimental section

GO films were prepared by the drop casting of a graphene oxide water dispersion at 0.4 wt% (Graphenea@) [26] on suitable substrates, at room temperature in air and at 1 atm pressure as presented in a previous paper [27]. They were dried in air for 24 h without thermal treatments.

The GO film shape, 10 µm in thickness, was circular with about 1 cm diameter. Figure 1 shows the SEM (Scanning Electron Microscope-QUANTA FEG450) (a) and AFM (Atomic Force Microscope—NANOSURF AG) (b) images of the prepared GO film indicating a uniform surface

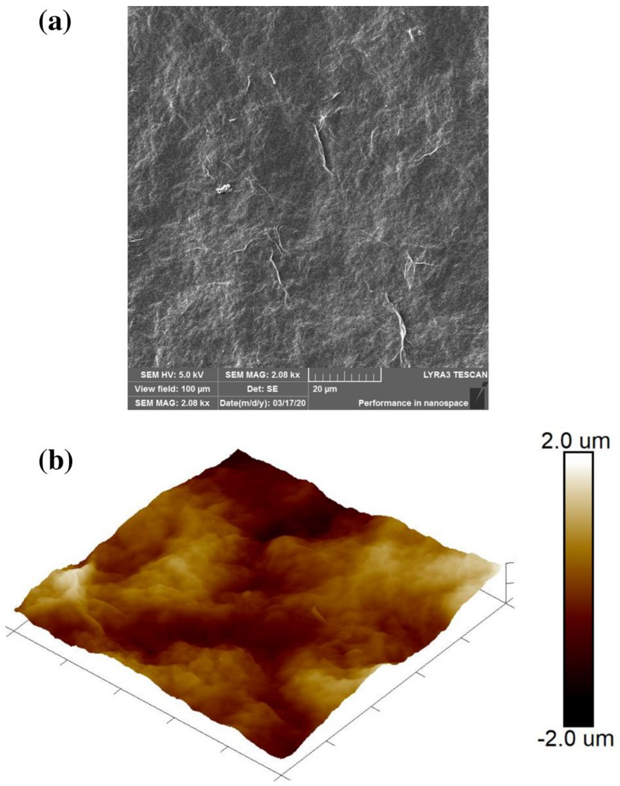

Fig. 1 Microscopy SEM (**a**) and AFM (**b**) of the GO film surface morphology

morphology with a sub-micrometric roughness. Cleaned and very polished Cu and Au supports (1 mm in thickness) were used as substrates for the drop-casted GO films. Conductive and high density silver paint was employed to realize the electrical contacts on both the metal surface and the GO film one. The Ag/GO/Ag contact is ohmic as reported in the literature [6].

Figure 2 shows the photos of two GO films deposited on the Cu (*a*) and Au (*b*) substrates. The electrical contacts on GO and Cu with Ag paint are shown in Fig. 2c together with the electrical connection copper wires. The GO/Cu junction is also displayed in presence of high relative humidity created by the water in a near beaker (*c*) and together with the Aosong AM2302 hygrometer used for the calibration (Fig. 2d).

A Keithley Source-Measure unit, mod. 236, was used for producing voltage and measuring current or vice versa. A Lake Shore 330 digital temperature controller, equipped with a platinum sensor, was used to measure the sample temperature. A commercial AM2302 hygrometer provided the RH content as a percentage (i.e. RH %). This value corresponds to the ratio of the actual atmospheric water vapour concentration to the equilibrium vapour concentration at a given temperature and pressure [23]. This low size device (about 1.3 cm × 5.8 cm × 0.7 cm), shown in the photo of Fig. 2d near to the prepared GO/Cu junction, gives a RH value in the (0–100%) range. It operates in the temperature range from − 40 to 80 °C, with a ± 2% RH accuracy, a sensitivity of 0.1% RH and a repeatability 0.1% RH [28, 29]. A PC computer collected all the data by means of an IEEE 488 interface and displayed the junction open-circuit voltage or short-circuit current together with the relative humidity as a function of the time in real time. I–V characteristics of the GO/Cu and GO/Au junctions were also investigated using the Keithley 236 Source-Measure unit. Measurements were performed in air, at 1 atm pressure and at room temperature.

Our attention was focalized on the GO/Cu junction sample with respect to the GO/Au one because of its low cost, good GO/Cu adhesion and electrical response. To calibrate the GO/Cu sensor, the obtained values were compared to the digital AM2302 RH values. Measurements were performed in the laboratory in free air by checking temperature and pressure and with a relative humidity level ranging from 50 to 100%. In this preliminary experiment, we did not use methods to reach RH levels less than 50%.

3 Results and discussion

3.1 The GO/metal junction electrical properties

We found that the GO/metal adhesion depends on many factors, such as the deposition temperature, metal surface roughness and cleaning, contact geometry, surface wetting and chemical reactivity, oxide formation at the interface. Both the realized GO/Au and GO/Cu junctions show a good adhesion.

The GO/Au and GO/Cu junctions show a contact potential mainly due to the Au or Cu substrate and GO-deposited film work functions. The work function values of Cu and Au are 4.65 eV and 5.1 eV, respectively [30]. GO is a low conducting semiconductor with a work function of about 5.3 eV [31] On the basis of the above mentioned work function values, at the GO/metal interface electrons from the metal can drift towards GO and can be trapped in GO producing a junction potential (positive metal and negative GO).

Figure 3a reports the room temperature I–V measurements on the GO/Cu junction performed in air at 1 atm and at 50% RH. The GO/Cu junction exhibits a very high resistance of about 11.86 MΩ ($R_d = 1$ V/84.3 nA) when the GO potential is positive with respect to Cu (direct bias). If the GO potential is negative with respect to Cu (reverse bias), the GO/Cu junction resistance is about 0.27 GΩ ($R_i = -1$ V/− 3.7 nA). The asymmetric I–V characteristic indicates that the GO/Cu junction is slightly rectifying. At zero current (open-circuit V_{oc}), the GO/Cu junction presents a positive potential barrier of about 47 mV, as shown in Fig. 3b. The voltage across the junction goes to zero at

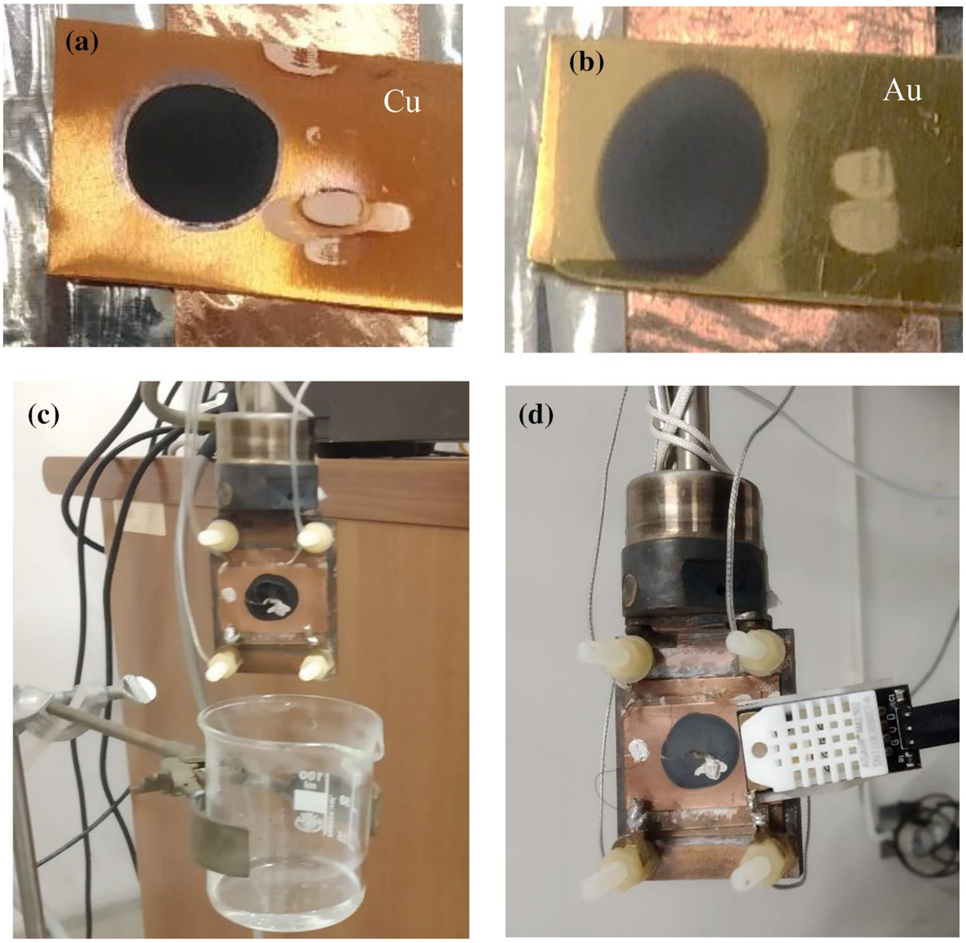

Fig. 2 Photos of GO films deposited on the Cu (**a**) and Au (**b**) substrates. Ohmic electrical contacts of Ag paint (**c**), GO/Cu junction in the presence of water vapour from a beaker (**c**) and during the calibration with the Aosong AM2302 hygrometer (**d**)

about − 0.126 nA (short-circuit current I_{sc}) as one can see in Fig. 3b. Really both the V_{oc} and I_{sc} values may change due to the temperature, air humidity and pressure, and presence of other gases (CO_2, O_2, H_2,…). The V_{oc} value is due to the exchange of electrons between the two materials. The electron transfer will occur predominantly from the conductor (Cu) with a lower work function to the GO material with a higher work function, justifying the V_{oc} positive value.

As a first approximation, neglecting the GO electron affinity, the V_{oc} value is equal to the difference in work functions of the two materials divided by the electron charge. Thus, since the work function of Cu at room temperature is $W(\mathrm{Cu}) = 4.65$ eV [30], the work function of GO can be calculated as follows:

$$W(\mathrm{GO}) = W(\mathrm{Cu}) + V_{oc} = 4.65\ \mathrm{eV} + 0.047\ \mathrm{eV} = 4.70\ \mathrm{eV} \quad (1)$$

a value in optimal accordance with that reported in the literature [32].

By changing the metal substrate on which the GO film is deposited, the measured V_{oc} value varies due to the different substrate work function and consequently the I–V characteristic curve of the studied junction changes too.

Figure 4 reports the comparison between the experimental I–V characteristics of the GO/Cu and GO/Au junctions (a) and a detail of the characteristics near to the zero of the two axes (b). The two characteristics are similar but some difference occurs. The measurements show that the GO/metal junction is rectifying in both two cases. In fact, in direct bias the resistance at + 1 V is about 11.86 MΩ and 61.38 MΩ for GO on Cu and Au, respectively, while, in reverse bias, at –1 V it is 270 MΩ and 83 MΩ for GO on Cu and Au, respectively. As one can see in Fig. 4b, the open-circuit voltages V_{oc} are about 47 mV and 180 mVf or the GO/Cu and GO/Au junction, respectively, while the short-circuit currents I_{sc} are about − 0.126 nA and − 1.3 nA in the two cases, respectively.

Using the literature data [30] for the Au work function $W(\mathrm{Au}) = 5.1$ eV, the approximated Eq. (1) gives $W(\mathrm{GO}) = 5.28$ eV. Thus, the GO work function is not well defined, being variable in the range between 4.70 eV and 5.28 eV in agreement with the literature [31, 32].

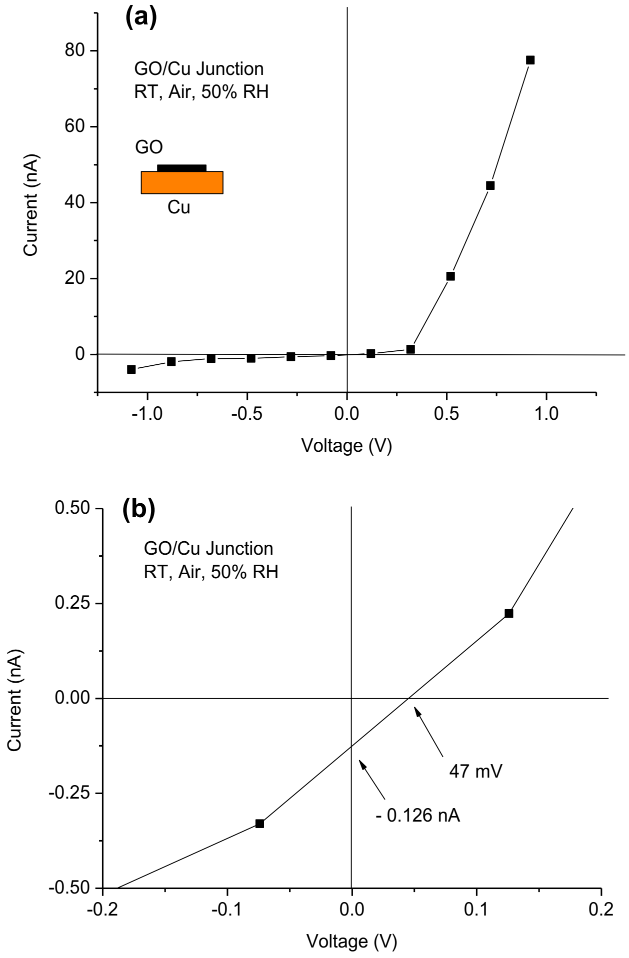

Fig. 3 I–V characteristics of the GO/Cu junction at room temperature and in air (**a**) and a zoom near to the axes zero (**b**)

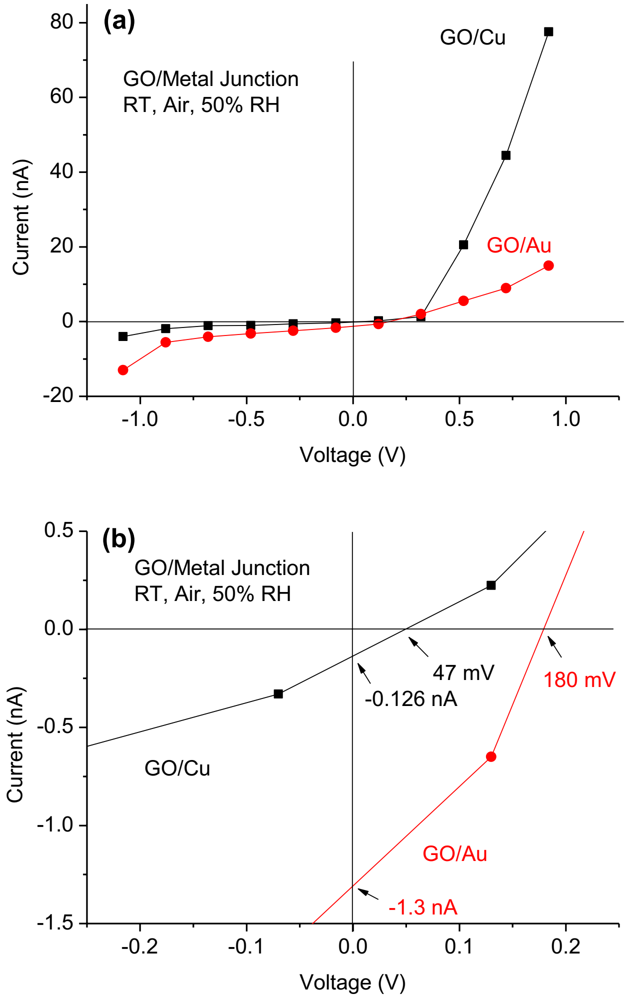

Fig. 4 Comparison between the experimental I–V characteristics of the junctions GO/Au and GO/Cu (**a**) and details of the characteristics near the zero of the axes (**b**)

3.2 The GO–Cu junction as water vapour detector

In order to monitor with a high sensitivity the electric charge exchange at the GO/Cu interface, we can either measure the open-circuit voltage V_{oc} or the short-circuit current I_{sc} as a function of the time, *t*. We have experimentally observed that in the presence of different humidity conditions, V_{oc} and I_{sc} change proportionally to the relative humidity level. Therefore, we studied the effect of RH on V_{oc} and/or I_{sc} measuring them in air at room temperature (291 K) and varying RH from 50 up to 80%. Since all our measurements start from medium humidity conditions (50% RH), the water molecules inside GO promote the ionic conduction by H^+. Increasing the humidity, the ionic conduction grows and so the apparent electrical conductivity. This happens because the number of conducting ions H_3O^+ grows with the content of water molecules which, penetrating between the GO layers, promote also the hydrolysis of some functional groups such as carboxyl groups and so on [22, 23]. The different RH values were obtained by exposing the GO/Cu junction to human breathing of different intensity and duration or to water vapour coming from a water beaker as reported in the literature [23, 33].

An RH increment produces a positive enhancement of V_{oc}, as shown in Fig. 5a, going from about 47 mV up to about 60 mV at a RH change from 50 to 80%, respectively. This increment corresponds to a relative variation $\Delta V_{oc} = 27.7\%$ for a variation $\Delta RH = 60\%$. Being at medium–high humidity regime, it is due, on the basis on what said above, to the rise of ion charges (H_3O^+) in GO by the ionization of water molecules and hydrolysis of various oxygen functional groups.

Figure 5b shows the short-circuit current versus time, $I_{sc}(t)$, during a fast RH variation from a value of RH = 50% to an RH value of about 80%, as determined by the AM2302 hygrometer. The RH increment produces a negative enhancement of the I_{sc} current, which can be explained as follows: since we start from a medium humidity regime (RH = 50%), increasing the humidity degree up

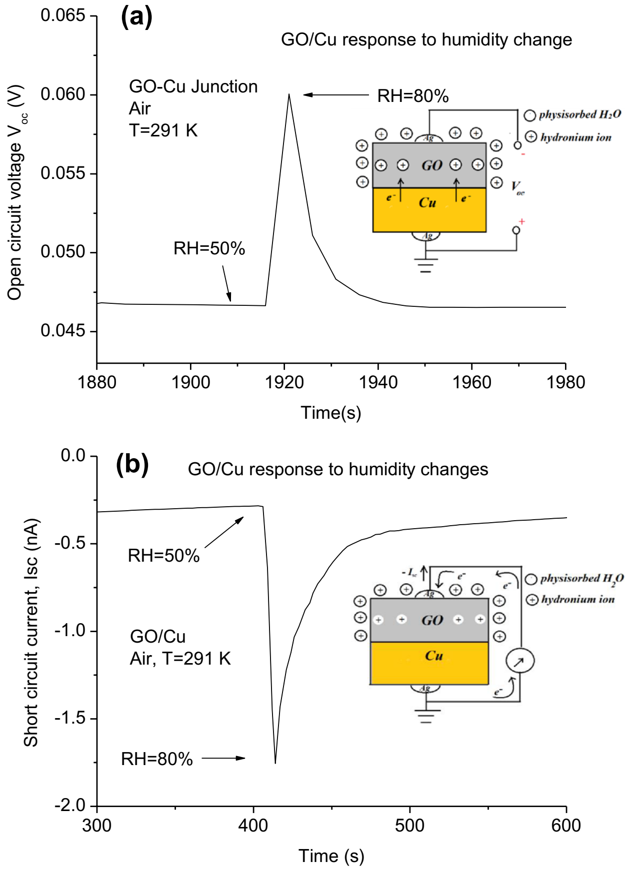

Fig. 5 Response of the GO/Cu junction to a fast increment of water vapour concentration measuring the V_{oc}(t) (**a**) and the $I_{sc}(t)$ (**b**) signals

to 80%, one or more layers of hydronium ions H_3O^+ form that attract electrons from the Cu metal. In this way, a negative current flows in the external circuit as shown in the scheme of Fig. 5b. In particular, for a RH change from 50 to 80%, the I_{sc} current changes from about − 0.29 nA up to − 1.74 nA, indicating a relative variation $\Delta I_{sc}\% = 500\%$ for a variation $\Delta RH = 60\%$. This result indicates that the I_{sc} monitoring is much more sensitive with respect to that of V_{oc} for the RH variation detection. Moreover, the plot of Fig. 5b shows that the response time of the I_{sc} signal is fast and of the order of seconds, while the recovery time is slower and of the order of 1 min (time to reduce the maximum intensity to a tenth value).

Figure 6 reports the typical examples of corresponding responses of the GO/Cu junction (ΔV_{oc}(*a*) and ΔI_{sc} (*c*) vs. *t*) and of the reference AM2302 hygrometer (*b, d*) to transient changes of water vapour concentration with respect to that of the surrounding environment, in the (58–100)% RH range. As previously said, the water vapour pulses were obtained either by placing a beaker containing water and water vapour near to the GO/Cu junction (Fig. 2c) or using fast exhaled human breath. The water vapour pulses were changed both in amplitude and duration.

3.3 The GO–Cu junction as a calibrated hygrometer

Tests were carried out to check the effectiveness of the GO/Cu junction as a calibrated hygrometer. In particular, the GO/Cu RH sensitivity was analysed and the performance of the GO/Cu sensor was compared and calibrated against the values given by the commercial Aosong AM2302 hygrometer [28, 29]. The two devices were placed very near to each other, as reported in the photo of Fig. 2d, to apply the same conditions of temperature and air pressure. Figure 7a reports the experimental relation between the ΔRH value obtained from the AM2302 hygrometer and the ΔV_{oc} signal given by the GO/Cu junction at 291 K in air. The relation between ΔV_{oc} and ΔRH is linear with experimental errors of about 10% for ΔV_{oc} and within 3% for ΔRH. On the basis of this linear relation, it is possible to calibrate the GO/Cu junction response with the RH level given by the AM2302 hygrometer.

In order to deduce information on the response time of the two sensors, Fig. 7b displays together the GO/Cu junction V_{oc} response (red curve) and the AM2302 RH% signal (black curve) in air at 291 K in the (0–1000) s time range. Both curves are obtained by changing the humidity level by means of exhaled human breaths, as previously reported in the literature [23, 33]. The comparison shows that the rise times in the GO/Cu and hygrometer are short and similar, suggesting that the physisorption of water molecules in the GO-based sensor is very fast. Furthermore, the recovery time in the GO/Cu junction is shorter than in AM2302, as shown in all peaks of Fig. 7b. For example for the peak at 531 s, characterized by a RH value of about 90%, the time required to decay to a ΔRH/10 value is about 36 s for AM2302 and about 7 s for the GO/Cu junction. Therefore, the GO-based sensor is about a factor five faster than the AM2302 sensor. In other words, this means that the desorption of water molecules from the GO-based sensor is faster than the used commercial hygrometer response. Of course a pile-up effect happens if a second humidity peak occurs before the full decay of the first one to the background value, indicating a limitation of the GO/Cu junction-based device at RH changes above about 0.14 Hz. Faster sensors can be obtained from thinner GO films. In fact when the GO film is on the order of 10 nm in thickness, the water molecule desorption occurs quickly (about 0.1 s) according to the literature [34].

Similarly to the previous case of the ΔV_{oc} versus ΔRH, Fig. 8 displays the GO/Cu junction short-circuit current variations, ΔI_{sc} versus the AM2302 sensor signal variations, ΔRH %. The error of measurements is within 15% for ΔI_{sc} and within 3% for ΔRH; within these errors the relation

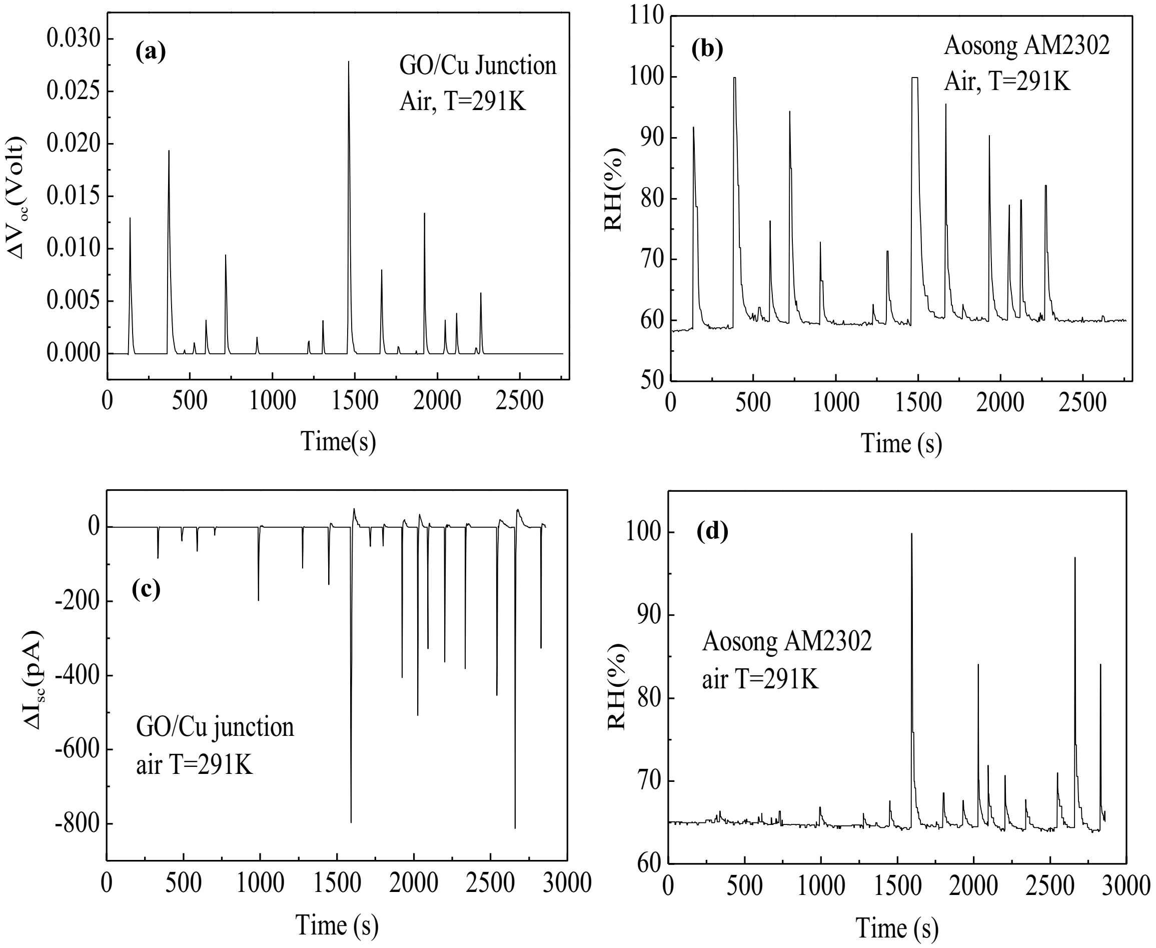

Fig. 6 Comparison between typical examples of response of the GO/Cu junction ($\Delta V_{oc}(t)$ (**a**) and $\Delta I_{sc}(t)$ (**c**)) and of the Aosong AM2302 hygrometer (ΔRH (t) (**b, d**)) to water vapour transient variations

ΔI_{sc} versus ΔRH is almost linear. The measure of ΔI_{sc} is to be preferred to that of ΔV_{oc} since, as mentioned above, this signal is much more sensitive to changes in RH %.

Further studies will be carried out in order to verify the interplay between temperature and RH variations. Moreover, the humidity effect on the structural stability of the obtained device will be also investigated.

4 Conclusions

In this paper, we have shown how a humidity sensor can be obtained from a GO/Cu junction.

The humidity response of the open-circuit voltage V_{oc} and the short-circuit current I_{sc}, of the GO/Cu interface, is directly dependent on the amount of relative humidity, i.e. on the quantity of the physisorbed water molecules. In fact in GO, electronic and ionic conduction mechanisms are present in different percentages depending on the degree of humidity.

The GO/Cu junction-based sensor can be used in a wide humidity range without an external bias but simply measuring the open-circuit voltage or the short-circuit current.

The sensor has short rise time of the order of one second and good reproducibility, errors within 15%, low size, simple realization and low cost.

Of course the GO/metal proposed device can be further improved, for example in the response velocity by reducing the GO thin-film thickness so to desorb the water molecules quickly. Moreover, the electrical signal amplitude can be increased by changing the substrate from Cu to Au with a V_{oc} increment of about a 3.8 factor.

Further characterization of the GO/Cu sensor will be performed; a permeable to water polymer covering of the device will be also proposed, and further developments of the GO/metal contact junction studies will be undertaken to improve the proposed sensor, which may have many applications in different scientific, environmental and industrial fields.

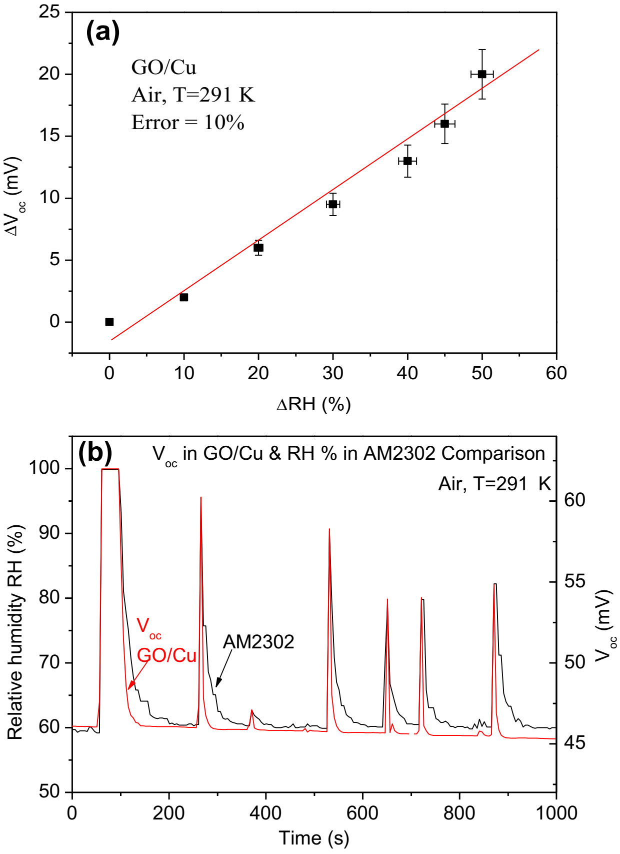

Fig. 7 ΔV_{oc} versus relative humidity variation ΔRH (**a**) and comparison of the GO/Cu junction $V_{oc}(t)$ response and of the AM302 hygrometer RH% signal in the (0–1000) s time range (**b**)

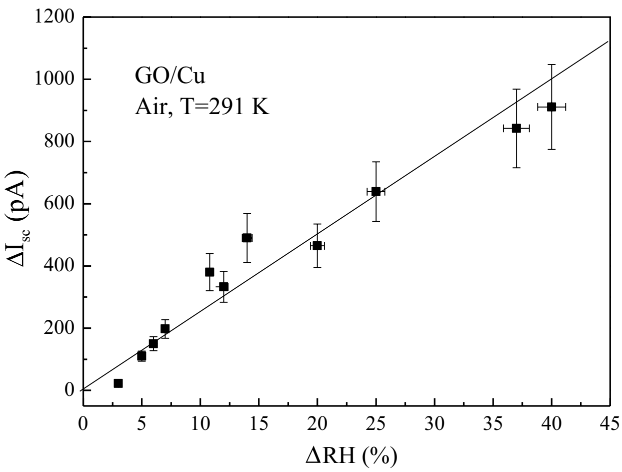

Fig. 8 Linear trend between the ΔI_{sc} versus ΔRH values

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