Proceedings

A Graphene Oxide Flexible Sensor for Humidity Detection †

Anna Maria Laera [1], *****, **Gennaro Cassano** [1], **Emiliano Burresi** [1], **Maria Lucia Protopapa** [1] **and Michele Penza** [1]

[1] ENEA-Italian National Agency for New Technologies, Energy and Sustainable Economic Development, Laboratory Functional Materials and Technologies for Sustainable Applications, Brindisi Research Centre, Strada Statale 7, Appia, Km. 706, I-72100 Brindisi, Italy; gennaro.cassano@enea.it, emiliano.burresi@enea.it, lucia.protopapa@enea.it, michele.penza@enea.it
* Correspondence: annamaria.laera@enea.it; Tel.: +39 0831 201588
† Presented at The 2nd International Electronic Conference on Chemical Sensors and Analytical Chemistry, online, 16-30 September 2023.

Abstract: A flexible humidity sensor operating at room temperature was produced by direct drop casting of a graphene oxide (GO) water solution on a substrate of bimatted polyester, previously coated with inkjet-printed interdigitated electrodes in silver. The GO was synthesized by using a modified Hummers' method, followed by an alkaline treatment with a water solution of KOH. Changes in the device resistance were measured for varying relative humidity in the range from 15% to 70% in a sealed stainless cell. The device showed high sensitivity, good repeatability, and fast recovery time. Being flexible and robust, the proposed sensors could be easily integrated into wearable equipment.

Keywords: graphene oxide; humidity sensors; flexible sensors; wearable devices

1. Introduction

The humidity sensors are among the most used devices not only in the industry of heating, ventilation, and air conditioning (HVAC), but also in many different fields such as biomedical, food processing, pharmaceutical, meteorology, microelectronics, and agriculture. The humidity control allows either to preserve comfortable and healthy environments, or to furnish efficient background to many industrial processes [1]. For instance, the production, transportation and storage of food and medicines requires controlled relative humidity values. Similarly, in semiconductor and electronics industry the performance of produced devices often depends on the humidity [2,3]. Examples of new application areas for humidity sensor are the wearable devices, the structural health monitoring, or the robotic smart skin [4,5]. The required key future for these emerging applications is flexibility, achieved through choosing suitable sensing layers and substrates.

In the present work a flexible humidity sensor operating at room temperature was obtained by drop casting of a graphene oxide (GO) water solution on silver interdigitated electrodes, previously inkjet printed on sheets of bimatted polyester. The GO is a 2D material flexible, stretchable, thermally stable, mechanically strong, lightweight, and biocompatible. The thickness of GO single atomic layer is approximately 1 nm, while the lateral length can reach micrometers. The potential of GO in designing efficient humidity sensors was firstly demonstrated by Yao and coworkers that developed a quartz crystal microbalance and a stress-based device [6,7]. An extremely sensitive GO-based capacitive sensor was fabricated by Bi and coworkers, who attested excellent performance along with rapid response and recovery times and long-term stability [8].

GO can be easily produced by using the Hummers and Offeman method which foresees graphite exfoliation and oxidation with permanganate [9]. However, the accurate e precise choice of experimental conditions is crucial because the sensing capability

and electrical properties vary from case to case depending on synthesis procedure, purity, presence of defects or oxidation degree. We adopted a modified Hummers' method, followed by an alkaline treatment with a water solution of KOH able to induce a partial deoxygenation. With respect to hydrazine and sodium borohydride, chemical reduction with KOH is less efficient, but advantageous for sensor design allowing either to improve electrical conductivity or to preserve more oxygenated functional groups, that are the major adsorption sites for water molecules.

The proposed device showed high sensitivity, good stability, and fast recovery time. For comparison an analogous device was fabricated by using a water solution of commercial GO. Due to the capability to furnish repeatable response at room temperature, the easy fabrication process, the high elasticity and robustness, the described sensors could be easily integrated into wearable equipment.

2. Materials and Methods

2.1. GO sythesis

All the reagents required to synthesize GO were purchased from Sigma-Aldrich and used without further purification. A concentrated water solution of H_2SO_4 (23 ml at 96% in weight) was added in a flask containing graphite. The resulting mixture was cooled down by using an ice bath and 3 g of $KMnO_4$ were added in little aliquots under vigorous stirring. After removal of the ice bath, 140 ml of deionized water and 10 ml of H_2O_2 were slowly added. The GO brown-yellowish powder was separated by centrifugation (4000 rpm for 10 min) and was washed three times with a water solution of HCl having a concentration of 10% in volume. Finally, an alkaline treatment was performed washing the GO powder (100 mg) with a water solution of KOH (10 ml at 10% in weight).

FTIR spectra were acquired with a Nicolet™ iS50 spectrometer, compressing the obtained dried powder in KBr pellets.

2.2. Chemiresistive device fabrication

For devices fabrication, the sheets of bimatted polyester were aligned under a photomask, previously impressed by screen printing with a bromograph. A silver based conductive ink was applied and cured at high temperature. Interdigitates electrodes with line and span width of 0.4 mm were produced. Each electrode had 7 lines distributed on a total area of 11.2 x 10 mm. Figure 1(a) shows a schematic design of the printed interdigitated electrodes. On the back of the polyester sheet, a heating circuit was inkjet printed by using graphite-based ink. This circuit was used to stabilize the resistance values of the GO coatings immediately after deposition by heating to a temperature of 50 °C.
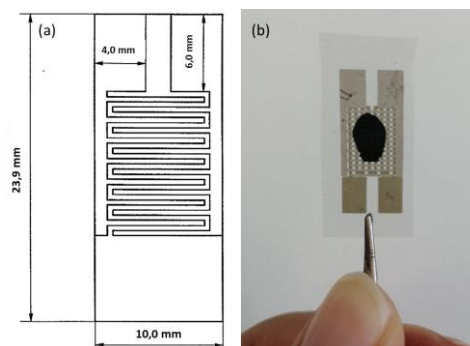

Figure 1. (a) Schematic of interdigitated electrodes and (b) digital photograph of GO coated device.

Two types of GO were tested, the first one purchased from Sigma Aldrich and used without further purification (product number 777676), and the second one synthesized by the above-described method. The dropped volume was in both cases 200 μl. Figure 1(b) shows GO coated interdigitated electrodes.

2.3. Experimental setup for gas sensing measurements

The two obtained devices were simultaneously located in a sealed stainless with a volume of approximately 500 cc. Each vapor test was performed by passing a carrier gas (dry air) controlled flow in a glass cylinder containing water at room temperature. An additional dry air steam was used to tune dilution of saturated stream. Changes in the device resistance were measured for varying relative humidity in the range from 15% to 70% by the volt-amperometric technique in the two-pole format by the multimeter (Agilent 34401A). The chemiresistor devices were automatically scanned by a switch system (Keithley 7001) equipped with a low-current scanner card (Keithley 7158) with a multiplexing read-out. All data were acquired and stored in a PC-based workstation equipped with software compiled in Agilent-VEE using an USB-GPIB interface-card (Agilent, 82357A). The relative humidity values were monitored by using a Vaisala humidity and temperature probe. All the exposures to wet air were conducted at room temperature. The sensing cycle consisted of three steps: i) a period of 60 min upon dry air flowing to reach a stable value of resistance; ii) an exposure time of 10 min to various relative humidity values; and finally, iii) a recovery time of 50 min under dry air flux to restore the starting value of resistance.

3. Results and Discussion

The GO surface is characterized by the presence of several chemical groups such as carboxyl (−COOH), hydroxyl (−OH), epoxy (C−O−C), carbonyl (−C−OH), ketone (−C=O), and 5- and 6-membered ring lactols (O−C−O). These groups are the major sites of water interaction, mainly through hydrogen bond formation [10].

The presence of −OH groups was attested by the appearance of a characteristic broad absorption band at 3380 cm^{-1} in the FTIR spectra shown in Figure 2.
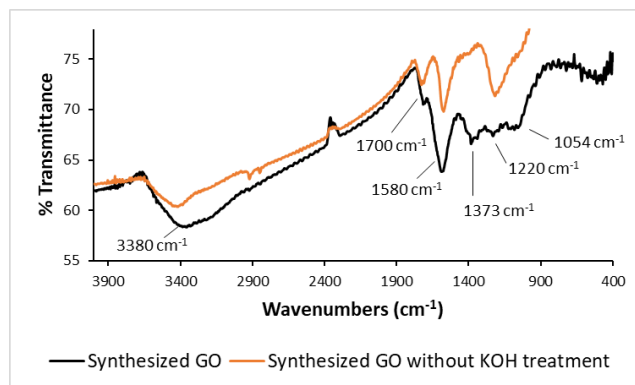

Figure 2. FTIR spectra of synthesized GO after KOH treatment (black line) and GO before KOH treatment (orange line).

The effects of the basic treatment with a water solution of KOH clearly emerge in FTIR spectra reported in Figure 2 for synthesized GO after KOH treatment and for the same sample before basic cleavage. The peak at 1700 cm^{-1}, due to -C=O stretching vibration, reduced in intensity following basic treatment, while the peak at 1580 cm^{-1}, due to aromatic stretching vibration of C=C bonds visibly increased. As expected for a reducing process, new sp^2 carbon atoms were introduced extending the graphene moieties. The FTIR signals at 1373, 1220 and 1054 cm^{-1} arise from -C-OH stretching, C-O-C stretching and C-O stretching, respectively. According to the literature, the mild reduction process performed with a basic solution mainly induces the removal of carbonyl groups and the resulting GO preserves above all epoxide and hydroxyl groups [11].

The synthesized partially reduced GO, deposited on the described flexible devices, was exposed to wet air in the relative humidity range 15-70% at room temperature, and

some typical responses are shown in Figure 3. A drastic decrease of electrical resistance was observed at increasing relative humidity.
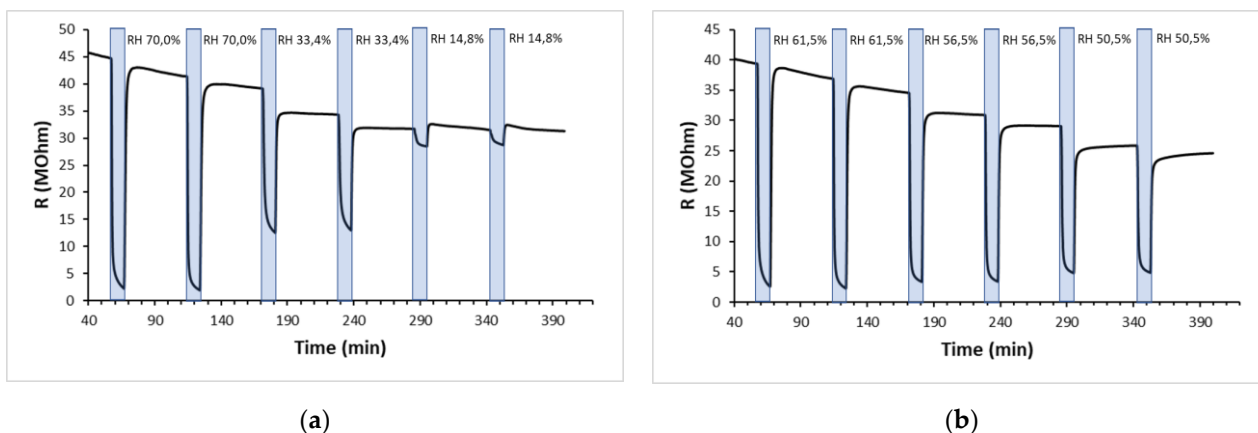

(**a**) (**b**)

Figure 3. Sensor resistance versus time upon exposure of decreasing relative humidity values in the range (a) 70.0-14.8%, and (b) 61.5-50.5%.

The responses were very reproducible and stable in time, but a partial recovery showed that the resistance values resulted lower than the starting resistance, indicating uncomplete removal of water molecules from sensing layer.

The sensor responses were calculated by the following relationship:

$$S\ (\%) = \left(\frac{R_g - R_a}{R_a}\right) x\ 100, \tag{1}$$

where R_g and R_a are the electrical resistance measured upon exposure to wet air and dry air, respectively. In Figure 4 the sensor responses of synthesized GO and commercial GO were compared. Higher sensitivities were measured with synthesized GO within the considered humidity range.
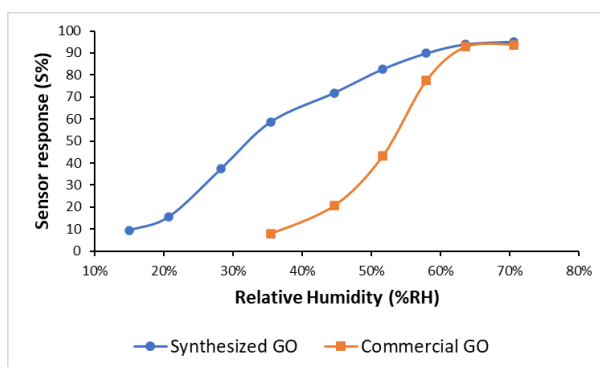

Figure 4. Sensor response as a function relative humidity of synthesized and commercial GO.

At low values of relative humidity, the increase of sensor response with relative humidity is mainly due to physiosorbed water molecules. In this regime the amount of adsorbed water molecules is not enough to allow the hopping transfer of protons between adjacent hydroxyl groups [7]. In addition, the formation of relatively strong hydrogen bonds with GO oxygenated groups restricts the mobility of adsorbed water molecules. In consequence the measured GO resistances resulted very high. Increasing the relative humidity, the water molecules interact either with oxygenated groups on GO surface or with other adsorbed water molecules forming a second adsorbed layer in which they preserve higher mobility. In this regime the conductivity generated by the Grotthuss chain reaction ($H_2O + H_3O^+ \leftrightarrows H_3O^+ + H_2O$) induces a drastic decrease of elec-

trical resistance. At the values of relative humidity higher than 65%, the sensitivity does not change significantly. In this regime water molecules deeply penetrate between GO layers and the resulting increased interlayer distance negatively affect the resistance values [12].

The recovery time, defined as the time required to return to 90% of the original resistance after removal of wet air, resulted in 40 and 70 sec for synthetized and commercial GO, respectively.

Although the responses of the sensors remain stable over time, a decrease of the GO baseline resistances was observed over six months indicating structural and chemical changes in the active layer. In future, to understand the chemistry of GO exposed to external stimuli such as light, humidity or temperature will be crucial to improve GO-based devices.

4. Conclusions

In summary, we have fabricated a chemiresistive flexible humidity sensor by using a thin GO active layer. Being rich in oxygenated functional groups, such as hydroxyl and epoxy groups, the GO can easily capture water molecules from external environment. When water concentration is sufficiently high, the conductivity generated by the Grotthuss chain reaction induce a drastic resistance decrease in GO thin film. Higher sensor performances in terms of sensitivity and recovery time were measured for synthesized GO with respect to commercial GO.

The good sensitivity, the responses repeatability at room temperature, the wide RH range detected, and the fast recovery time are the main advantages of the proposed humidity sensor. Furthermore, the flexibility, the easy fabrication process, the high elasticity, and robustness make the device easier to use in many emerging application areas, such as the wearable devices, the structural health monitoring, or the robotic smart skin. The disadvantageous aspects are related to deposition of GO film, because dropping a water solution with a pipette does not allow a strict control of thickness and roughness. The conductivity of resulting GO films significantly changed within thickness. In addition, after the recovery run the resistance values resulted lower than the starting resistance, indicating a partial removal of water molecules from sensing layer. Furthermore, a decrease of the GO baseline resistances was observed over a period of six months indicating structural and chemical changes in the active layer. To control structure, chemical stability, and properties of GO by choosing the suitable procedure of synthesis and purification will be crucial to improve the performance of GO-based devices.

References

1. Zang, D.; Wang, M.; Tang, M.; Song, X.; Zhang, X.; Kang, Z.; Liu, X.; Zhang, J.; Xue, Q. Recent progress of diversiform humidity sensors based on versatile nanomaterials and their prospective applications. Nano Res. **2022**. https://doi.org/10.1007/s12274-022-4917-y

2. Penza, M.; Cassano, G. Relative humidity sensing by PVA-coated dual resonator SAW oscillator. *Sens. Actuator B Chem.* **2000**, *68*, 300-306. https://doi.org/10.1016/S0925-4005(00)00448-2

3. Ascorbe, J.; Corres, J. M.; Arregui, F. J.; Matias, I. R. Recent developments in fiber optics humidity sensors. *Sensors* **2017**, *17*, 4, 893. https://doi.org/10.3390/s17040893

4. Delipinar, T.; Shafique, A.; Goahr, M. S.; Yapici, M. K. Fabrication and materials integration of flexible humidity sensors for emerging applications, *ACS Omega* **2021**, *6*, 13, 8744-8753. https://doi.org/10.1021/acsomega.0c06106

5. Tai, H; Duan, Z.; Wang, Y.; Wang, S.; Jiang, Y. Paper-based sensors for gas, humidity, and straion detection: a review. *ACS Appl. Mater. Interfaces* **2020**, *12*, 31037-31053. https://dx.doi.org/10.1021/acsami.0c06435

6. Yao, Y.; Chen, X.; Guo, H.; Wu, Z. Graphene oxide thin film coated quartz crystal microbalance for humidity detection. *Appl. Surf. Sci.* **2011**, *257*, 7778-7782. https://doi.org/10.1016/j.apsusc.2011.04.028

7. Yao, Y.; Chen, X.; Guo, H.; Wu, Z.; Li, X. Humidity sensing behaviors of graphene oxide-silicon bi-layer flexible structure. *Sens. Actuators B Chem.* **2012**, *161*, 1053-1058. https://doi.org/10.1016/j.snb.2011.12.007

8. Bi, H.; Yin, K.; Xie, X.; Ji, J.; Wan, S.; Sun, L.; Terrones, M.; Dresselhaus, M. S. Ultrahigh humidity sensivity of graphene oxide. *Sci. Rep.* **2013**, *3*, 2714. https://doi.org/10.1038/srep02714

9. Hummers, W.S.; Offeman, R.E. Preparation of graphene oxide. *J. Am. Chem. Soc.* **1958**, *80*, 1339.

10. Mouhat, F.; Coudert, F.X.; Bocquet, M.L. Structure and chemistry of graphene oxide in liquid water from first principles. *Nat. Commun.* **2020**, *11*:1566. https://doi.org/10.1038/s41467-020-15381-y

11. Zhu, J.; Xiao, X.; Zheng, K.; Li, F.; Ma, G.; Yao, H. C.; Wang, X.; Chen, Y. KOH-treated reduced graphene oxide: 100% selectivity for H_2O_2 electroproduction. *Carbon* **2019**, *153*, 6-11. https://doi.org/10.1016/j.carbon.2019.07.009

12. Naik, G.; Krishnaswamy, S.; Room-temperature humidity sensing using graphene oxide thin films. *Graphene* **2016**, *5*, 1-13.