proceedings

MDPI

Abstract

Graphene oxide-based flexible sensors for detection of volatile organic compounds at room temperature †

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, Brindisi Research Centre, S.S. 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.: 0831201588

† Presented at the Eurosensors XXXIV, Lecce, Italy, 10-13 September 2023.

Abstract: Flexible sensors, with an active layer made of graphene oxide (GO), were produced to detect volatile organic compounds (VOCs) at room temperature. Copper interdigitated electrodes were inkjet printed on a substrate of bimatted polyester and the direct drop casting of a GO water solution allowed the device coating. The performance of both commercial GO and GO synthesized by a modified Hummers' method was investigated and compared. The oxygenated functional groups on GO surface mainly enhance the selective sensing of polar analytes. The fabricated sensors exhibit the highest response towards alcohols, and minor sensitivity to esters, ketones, ethers and apolar petroleum ether.

Keywords: graphene oxide; volatile organic compounds; wearable sensors

1. Introduction

Volatile organic compounds (VOCs) are common and widespread air pollutants of both indoor and outdoor environments. In consequence, the detection and monitoring of VOCs has attracted the attention of numerous researchers in the field of environmental protection. The development of efficient portable or wearable sensors to detect VOCs would allow to overcome the problems associated with the usually used gas chromatography, which guarantees high performance, but requires expensive equipment with complex sampling and analysis procedures. Graphene related 2D materials are a convenient choice to design wearable devices being flexible, stretchable, thermally stable, mechanically strong, lightweight, and biocompatible [1]. In particular, the use of GO as sensing material has gained increasing interest in recent years, due to the capability of oxidized area to act as adsorption site for analytes [2].

We propose flexible sensors obtained through the drop casting of GO water solutions on copper interdigitated electrodes, previously inkjet printed on sheets of bimatted polyester. The performances of commercial GO and GO produced by a modified Hummers' method were investigated to correlate structural properties and device sensitivity. The fabricated sensors exhibit the highest response towards alcohols, such as ethanol and isopropanol, although they are also able to detect esters, ketones, ethers and apolar petroleum ether with minor sensitivity.

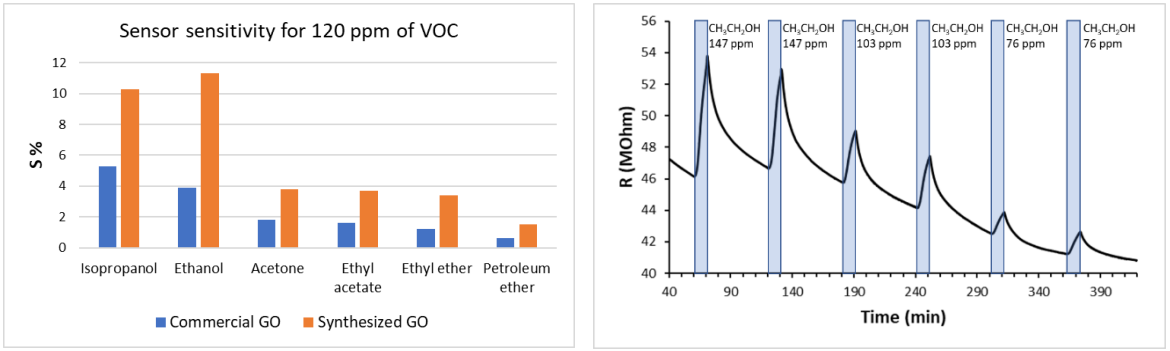
2. Materials and Methods

Copper interdigitated electrodes were injected printed on flexible polyester sheets and coated with an active layer of GO by drop casting of a water solution with a concentration of 2 mg/ml. The dropped volume was set to 10 µl. Two types of GO were investigated, the first one purchased from Sigma Aldrich and used without further purification, and the second one synthesized by a modified Hummers' method. The fabricated devices, having size 1 x 2 cm, were exposed to several dilutions of gas analytes in a sealed stainless cell. Each vapor test was performed by passing a carrier gas (dry

air) controlled flow in a glass cylinder containing the liquid analyte at room temperature. An additional dry air steam was used to tune dilution of saturated stream.

3. 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). The performed tests attested that the major absorption sites for analytes are specifically the oxygenated polar group, since the sensors response is significantly reduced as the polarity of the analytes decreases as shown in Figure 1a.



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

Figure 1. (**a**) Sensor response towards several VOCs with different dipole moment; (**b**) Sensor resistance versus time upon exposure of decreasing ethanol concentration of 147, 103 and 76 ppm.

The sensor responses were calculated by the following relationship:

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

where R_g and R_a are the electrical resistance measured with exposure to gas and air, respectively. In Figure 2b sensors response towards ethanol are reported, as example, in the concentration range 147 - 76 ppm. The resistances values increase in presence of alcohol as expected for a p-type semiconductor. Repeated cycling tests, performed in a period of six months, attested the long-term stability of the GO active layer. Due to the capability to furnish repeatable response at room temperature, the easy fabrication process, the high elasticity and robustness, the described sensors could lead to implementation of flexible wearable devices for air quality monitoring and chemical sensing.

Author Contributions: Conceptualization, A.M.L. and M.P.; methodology, G.C. and M.P.; formal analysis, E.B. and M.L.P.; investigation, A.M.L., E.B. and M.L.P.; resources, G.C. and M.P.; data curation, A.M.L. and M.P..; writing-original draft preparation, A.M.L. and M.P.; writing - review and editing, A.M.L. and M.P.; supervision, M.P.

Acknowledgments: The authors would like to thank BIOAGE agency for copper interdigitated electrodes fabrication by using photolithographic printing techniques.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Singh, E.; Meyyappan, M.; Nalwa, H.S. Flexible graphene-based wearable gas and chemical sensors. *ACS Appl. Mater. Interfaces* **2017**, *9*, 34544-34586. https://doi.org/10.1021/acsami.7b07063.
2. Toda, K.; Furue, R.; Hayami, S. Recent progress in applications of graphene oxide for gas sensing: a review. *Anal. Chim Acta* **2015**, *878*, 43-53. https://dx.doi.org/10.1016/j.aca.2015.02.002.