Wireless Monitoring of Breath by means of a Graphene Oxide-based Radiofrequency Identification Wearable Sensor

M. C. Caccami, M. Y. S. Mulla, C. Di Natale, and G. Marrocco
University of Rome Tor Vergata, Via del Politecnico, 1, 00133, Rome (ITALY)

***Abstract*—The monitoring of the breathing dynamic characteristics, including the presence of biomarkers in exhaled breath, is of growing interest in noninvasive diagnosis of diseases. We describe a wearable radiofrequency identification (RFID) device hosting a flexible antenna suitable for integration into a facemask and a sensor made of graphene oxide sensitive to the humidity variations. The so obtained wearable wireless sensor was characterized in reference conditions and was then experimentally demonstrated to be capable of detecting the inhalation/exhalation cycles and abnormal patterns of respiration like the apnea by measuring the changes in graphene oxide resistance.**

***Index Terms*—Graphene, RFID sensing, Wireless breath sensor**

I. Introduction

Breath analysis is recognised as an useful indicator of a person's health status [1]. Monitoring the respiratory rate and pattern of both healthy and stressed/unhealthy individuals indeed enables an early detection of diseases and disorders, such as sleep apnea and cardiac arrest, and the characterisation of illnesses such as asthma or chronic obstructive pulmonary disease (COPD). Moreover, the identification of biomarkers and volatile organic compounds (VOCs) in exhaled breath is helpful in noninvasively diagnosing and monitoring of respiratory diseases such as lung cancer or ventilator-associated pneumonia (VAP). Nowadays, conventional methods of breathing monitoring involve bulky, inconvenient and often expensive equipments that are generally incompatible with flexible wearable formats. Specifically, they require the patient to attach an uncomfortable nasal probe or cannula and to wear a chest band and sensors. Wired connections to data acquisition system and the complex circuitry prevent a long-term use required for continuous monitoring, besides creating a discomfort for the subjects [2]. Wireless and multifunctional wearable devices, capable of performing multiple actions including sensing, actuation, data storage, and energy supply, could instead be a powerful tool to enable a continuous and comfortable monitoring of breath, suitable to advance large-scale and real-time studies of the physiological processes.

This contribution addresses the wireless breath monitoring by means of Radiofrequency Identification (RFID) platform which, as already demonstrated in several recent papers, is becoming a valuable technology for body-centric tracking and monitoring. In particular, the paper proposes the combined use of a flexible RFID device suitable for integration into a facemask and coupled with a nanomaterial sensor made of graphene oxide [3]. Graphene is a two-dimensional nanomaterial composed of a grid of carbon atoms with sensing capabilities. The intensive research interest on the wide range of bio-applications of graphene and its derivatives is due to its outstanding physical and chemical properties and, above all, to the intrinsic biocompatibility, low cost, and easy biological/chemical functionalization. The graphene oxide is well known to be very sensitive to water, thanks to the interactions between the exposed functional oxygen groups and water [4]. Thus, it can be considered as a promising receptor for use in wearable humidity sensors. Previous examples of sensors based on graphene functionalized with chemical/biological substances are discussed in [5] and [6], respectively for the detection of metabolites, such as the lactate, and of some pathogenic bacteria. The change in electrical conductivity of the graphene related to the variable parameter is modulated and monitored using an inductively coupled radiofrequency reader device. We demonstrate here the feasibility of a UHF RFID graphene oxide wireless sensor to capture the inhalation/exhalation cycles as well as anomalous events like the apnea. First a graphene oxide-based sensor of relative humidity (RH) is characterised and then the whole wireless sensor is described and demonstrated by means of experimental examples.

II. Graphene Oxide-based Sensor

The considered graphene oxide sensor (Fig. 1) is composed by a Si/SiO_2 wafer with parallel Au electrodes employed as substrate. $3\mu l$ of commercially available graphene oxide solution $(2mg/ml)$ was deposited over the electrodes by drop casting and left to dry at ambient conditions. While the graphene oxide solution was drying, $10V$ peak to peak alternating voltage with $1MHz$ frequency generated by function generator was applied between the electrodes. After complete drying, the substrate was annealed at $195°C$ for 15 minutes on hot plate in dark.

A. Humidity Sensing characterisation

The characterisation of the device as humidity sensor was based on the change in graphene oxide resistance due to the absorption and desorption of water vapour. In order to test the

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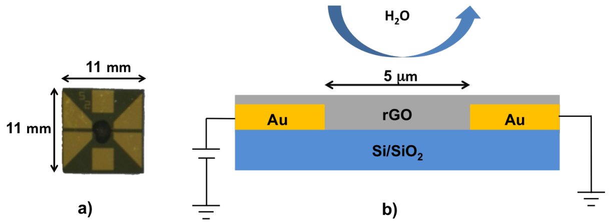

Fig. 1. a) Graphene oxide sensor and b) its schematic cross-section including a Si/SiO$_2$ with p-type doped silicon wafer ($300nm$ SiO$_2$ layer) and Au $20nm$ layer with $2nm$ chromium adhesion promotion layer.

recovery, reproducibility, and response speed to the gas under test, the sensor was exposed to cyclic increasing concentrations of humidity. In these measurements, the water molecules to be detected were separately vaporised with precisely dosed concentrations by means of a flow-system comprising a mass-flow controller (MKS Instrument inc.) and an airtight chamber, wherein the sensor was placed. The measurement protocol consisted to flow synthetic dry air through the system for 1 hour to establish a system baseline, then to flow the selected dry/humid air mixture at different concentrations for 30 minutes (exposure time) and subsequently to flow dry air to clean the sensor surfaces for 30 minutes (recovery time). The profile of the resistance variation vs. time with respect to the relative humidity changes from dry to saturation is shown in Fig. 2a. The resistance variation follows the typical exponential profile of adsorption/desorption process. The peaks are approximately proportional to the concentration of the humidity level. The reference humidity data during the measurements (Fig. 2b) are provided by the *Electronic Nose* sensor [7] used as hygrometer.

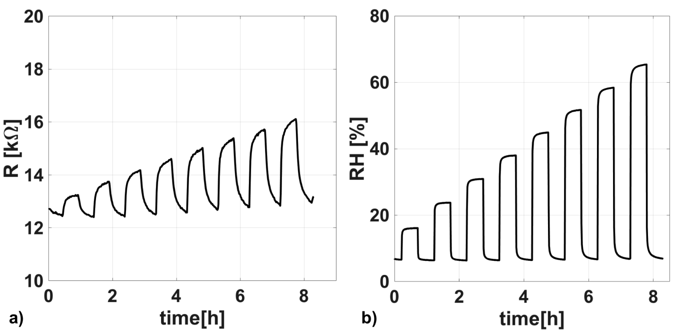

Fig. 2. a) Graphene oxide resistance variation vs. time when the humidity increases from the dry air value to the saturation, alternated with recoveries with dry air; b) the humidity data vs. time as detected by the *E-Nose*.

A drift phenomenon is visible in the graphene response thus revealing a slow recovery of the sensor to humidity. However, such a behavior could be also correlated to other factors, for instance, the condensation effect of the vapour water deposited on the surface of the graphene oxide layer during the cycle of measurement and the presence of possible leakages through the ducts of the mass-flow controllers. Fig. 3 shows the calibration curve of the sensor, i.e. the sensor resistance vs. the relative humidity variation. The profile appears almost linear with respect to the increasing moisture levels and it is therefore possible to extract the sensitivity of the sensor, i.e. the slope of the linearised curve, as the resistance difference generated by 1% change in the RH level:

$$S[R] = \frac{|\triangle R|}{|\triangle RH|} = \frac{|R(RH_{high}) - R(RH_{low})|}{|RH_{high} - RH_{low}|} = 60\Omega/RH. \tag{1}$$

In particular, the relative variation of the resistance is about $4k\Omega$ within humidity range from dry air to 66% RH.

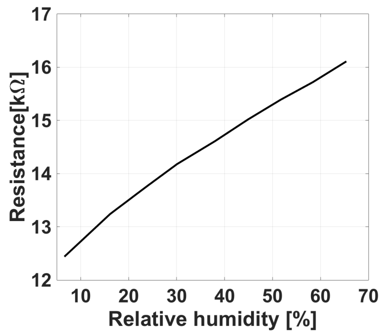

Fig. 3. The calibration curve $R \leftrightarrow RH$ corresponding to the response shown in Fig. 2a.

III. The RFID Antenna

The considered RFID antenna suitable to host the graphene oxide sensor is the Radio6ense Radio-board [8] (Fig. 4a) based on a configurable family of RFID transponders that provide the pure identification features as well as offer a native integrated electronics for sensing activities. The tag, manufactured over a flexible $50\mu m$-thick Kapton substrate, is comprised of a meander line antenna and a tunable spiral impedance transformer with the possibility of adding lumped elements such as inductors or additional metal stubs. The antenna is connected to the AMS SL900A microchip, which includes an Analog-to-Digital Converter (ADC) capable of controlling up to two analog external sensors and even an integrated temperature sensor with programmable dynamic range between -40/150°C. The radio-board antenna can be used *i)* in a fully passive mode, i.e. the energy required for activation and actions is entirely scavenged from the electromagnetic waves emitted by the remote interrogator, and *ii)* in battery-assisted mode, a local battery providing additional energy for improved read range and, above all, to perform periodic measurements even in absence of the reader (*data-logging* modality). For these preliminary experiments, the graphene oxide sensor was loosely integrated by connecting it to two input pins of the radio-board.

IV. Breathing Monitoring Experimentation

The resulting graphene oxide RFID sensor was conformed on the surface of a textile facemask to capture breathing sequences (Fig. 4b). The measurements were carried out through the *data-logging* modality activated by means of a portable reader (CAEN RFID qIDmini Keyfob Bluetooth UHF

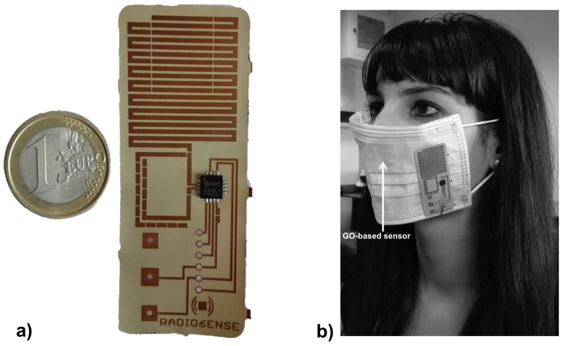

Fig. 4. a) Flexible antenna prototype on Kapton. b) Radio-board antenna and graphene oxide (GO) sensor integrated into a facemask.

RFID Reader). The results related to the resistance response of the sensor with respect to the different humidity levels were stored in the internal user memory of the microchip during the cycle of measurement and further analysed in post-processing. At the beginning, the sensor was exposed to the ambient humidity in order to establish a baseline value. Then, we asked a subject to wear the facemask and to continuously and deeply breathe through the nose for a few minutes. Fig. 5 depicts the change in graphene oxide resistance on exposure to breath.

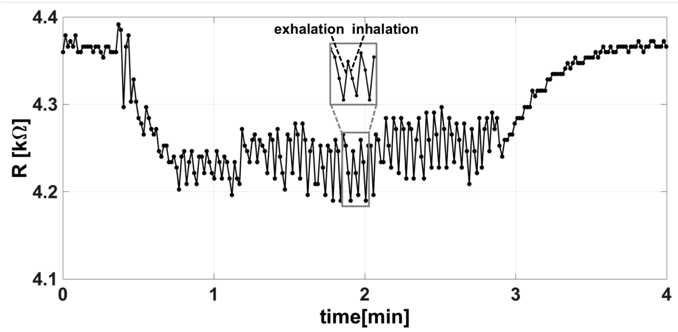

Fig. 5. The respiratory activity of a subject recorded using a facemask with the embedded graphene oxide sensor and the radio-board antenna.

The changes in resistance for each breath cycle are clearly detectable in comparison with the signal oscillations when the sensor is at rest. The estimated maximum dynamic range of the breathing signal (82Ω) is indeed much higher than the standard deviation value of the noise level (4Ω). In particular, during the breathing out, human breath is strongly humidified (RH>60%), and therefore the amount of water on the surface of the graphene oxide layer increases, and in turn its resistance. While, during the breathing in, the amount of water absorbed by the graphene oxide drop is reduced since the relative humidity of the surrounding environment is almost always lower than the exhaled air. Fig. 5 also shows the recovery capability of the graphene oxide sensor which tends to restore back to the baseline after the breathing cycle. Finally, we asked a subject to breathe with alternating short intervals of apneas. The measured resistance profile, shown in Fig. 6, emphasises the capability of the sensor to detect the breathing peaks compared to the condition of apnea.

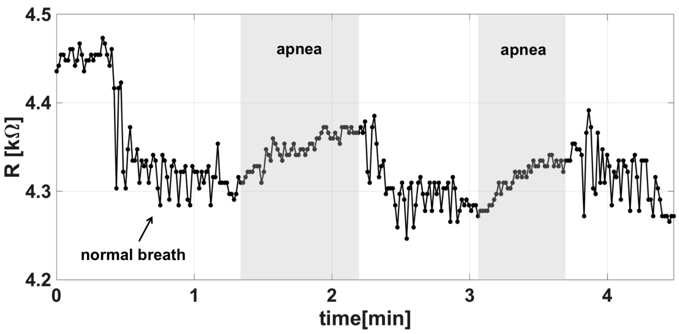

Fig. 6. The respiratory activity by repeating apneas with short intervals.

V. Discussion and Conclusion

In this contribution, the advantageous sensing capabilities and the hygroscopic character of the graphene oxide were exploited in order to introduce a new class of wireless wearable RFID sensors capable of monitoring different breathing patterns. It was demonstrated the possibility to correlate the effect of the resistance changes of the graphene oxide with the rate of respiration. Moreover, such a wearable RFID system may enable a simultaneous multiparameter sensing, in particular the humidity and temperature. In the next step of the research the wireless sensor will be implemented by means of the Epidermal technology so that the whole system comprising the antenna and the graphene sensor will be deposited over a thin membrane and directly stuck on the face close to the nose for a superior comfort of the user.

References

[1] A. Amann, W. Miekisch, J. Schubert, B. Buszewski, T. Ligor, T. Jezierski, J. Pleil, T. Risby, "Analysis of exhaled breath for disease detection", *Annual Review of Analytical Chemistry*, Vol. 7, pp 455–482, 2014.

[2] Firat Güder, Alar Ainla, Julia Redston, Bobak Mosadegh, Ana Glavan, T. J. Martin, and George M. Whitesides, "Paper-Based Electrical Respiration Sensor", *Angewandte Chemie International Edition*, Vol. 55, Issue 19, pp 5727 –5732, 2016.

[3] M. Zhang, R. R. Naik, L. Dai, "Carbon Nanomaterials for Biomedical Applications", Vol. 5, *Springer Series in Biomaterials Science and Engineering,* 2016.

[4] S.Borini, R. White, D. Wei, M. Astley, S. Haque, E. Spigone, N. Harris, J. Kivioja, and T. Ryhänen, "Ultrafast Graphene Oxide Humidity Sensors", *ACS Nano*, 7 (12), pp 11166–11173, 2013.

[5] P. Labroo, Y. Cui, "Flexible graphene bio-nanosensor for lactate," *Biosensors and Bioelectronics*, 41, pp 852–856, 2013.

[6] M.S. Mannoor, H. Tao, J.D. Clayton, A. Sengupta, D.L. Kaplan, R.R. Naik, N. Verma, F. G. Omenetto, M. C. McAlpine, "Graphene-based wireless bacteria detection on tooth enamel", *Nature Communications* 3, no. 763, 2012.

[7] R. Gasparri, M. Santonico , C. Valentini, G. Sedda, A. Borri, F. Petrella, P. Maisonneuve, G. Pennazza, A. D'Amico, C. Di Natale, R. Paolesse, L. Spaggiari, "Volatile signature for the early diagnosis of lung cancer", *Journal of Breath Research*, vol. 10, no. 1, 2016.

[8] C. Occhiuzzi, S. Amendola, S. Manzari, G. Marrocco, "RFID-based Multilevel Sensing Network for Industrial Internet of Things", submitted on *IEEE Internet of Things Journal*, under review.