A Networked Wearable Device for Chemical Multisensing

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Abstract The present contribution illustrates the early stage activities of the project CONVERGENCE FLAG-ERA H2020. The project is aimed at improving the quality of healthcare during active life by preventing the development of diseases through earlier diagnosis of cardiovascular and/or neurodegenerative diseases, and meets the growing desire of consumers for a deeper awareness of their conditions; indeed, the extensive availability of smartphones and tablets and the technology therein incorporated enable the monitoring and transmission of vital parameters from the body of a patient to medical professionals. CONVERGENCE extends this concept, aiming to create a wireless and multifunctional wearable system, able to monitor, in addition to key parameters related to the individual physical condition (activity, core body temperature, electrolytes and biomarkers), even the chemical composition of the ambient air (NO_x, CO_x, particles). Herein is summarized the project activity, which involves ENEA group together with CEA (Commissariat à l'Energie Atomique, France) and UCL (Université catholique de Louvain, Belgium).

Keywords Wearable · Environmental monitoring · Sensor · Internet of things

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B. Andò et al. (eds.), *Sensors*, Lecture Notes in Electrical Engineering 539,
https://doi.org/10.1007/978-3-030-04324-7_3

1 Introduction

Medical technologies include a variety of devices, such as pacemakers, defibrillators, deep-brain stimulators, insulin pumps, which aim at improving the quality of healthcare through non-invasive treatment of pathological conditions and/or earlier diagnosis. The extensive availability of smartphones and tablets is directing consumers towards wearable technologies, capable of monitoring and transmitting vital parameters from the body of a patient to medical professionals, thus preventing the development of diseases [1–4]. CONVERGENCE, a FLAG-ERA H2020 project, broadens this concept by realizing a wireless and multifunctional wearable system, able to monitor, in addition to key parameters related to the individual physical condition (activity, core body temperature, electrolytes and biomarkers), even the chemical composition of the ambient air (NO_x, CO_x, particles).

In this contribution we focused on the early stage of the project activities, which involves our group together with CEA (Commissariat à l'Energie Atomique, France) and UCL (Université catholique de Louvain, Belgium) and regards the implementation of a demonstrator composed by gas sensors integrated into a test platform realized by CEA. In the project framework, one of the tasks is to develop sensors for the detection of NO_2 based on graphene, a material widely known in the scientific literature for the specificity towards this pollutant [5–7]. The provided sensors, based on bare and ZnO nanoparticles decorated-graphene, are chemiresistive devices able to detect nitrogen dioxide in the range 100–1000 ppb. They were connected with an electronic board, developed for sensor data acquisition in real time; data were directly sent by Bluetooth on smartphones. Finally, a microarray platform made of micro-interdigitated electrodes, developed by UCL, will allow the miniaturization of the demonstrator in a post-CMOS process [8]. Detection limit below 100 ppb ($\geq$10 ppb), selectivity, ultra-low-power consumption (<20 μW continuously), and low-cost fabrication (<1 €/die), are the key challenges towards Internet-scale chemical sensing applications in environmental monitoring.

2 The Environmental Sensors

In line with the project requirements, ENEA labs worked on the synthesis of the functionalized material and its optimization, realizing chemiresistive devices based on bare and ZnO nanoparticles decorated-graphene, able to detect nitrogen dioxide at room temperature in the range 100–1000 ppb; pristine graphene (GR) was prepared by sonication assisted graphite exfoliation. Graphite flakes were dispersed into a mixture of ultrapure water and i-propanol (at 1 mg/ml) and sonicated in an ultrasonic bath for 48 h. Afterwards, graphite crystallites were removed by centrifuging for 45 min at 500 rpm. The concentration of the graphene suspension was 0.1 ± 0.1 mg/ml. The preparation of ZnO decorated graphene (GZnO) was performed by freeze drying of graphene suspension. 2.5 mg of graphene powder, mixed with 4 mg of ZnO (Ø 14 nm)

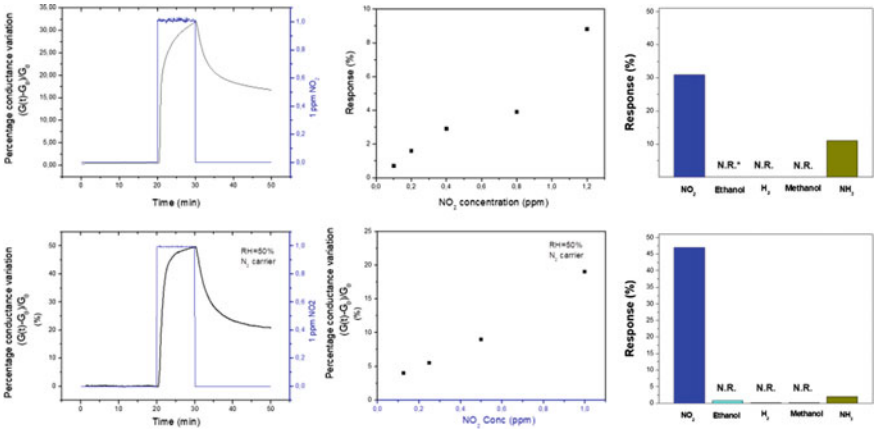

Fig. 1 Sensing responses to a single pulse of 1000 ppb NO_2 and relative sensitive curves of chemiresistors based on graphene (panel a) and ZnO decorated graphene (panel c). The selectivity towards 1 ppm NO_2, 50 ppm ethanol, 1% hydrogen (H_2), 50 ppm methanol and 250 ppm ammonia (NH_3) of chemiresistors based on graphene (b) and ZnO decorated graphene (d). *N.R. = No response

and microwave irradiated for 5 min at 1000 W. The resulting powder was dissolved in ethanol and the sensitive material was dispensed on interdigitated commercial macroscopic electrodes realized on alumina substrate for a preliminary test towards NO_2, whose results are illustrated in the Fig. 1.

As can be inferred from the graphs of Fig. 1, both preparations exhibit a high degree of specificity towards nitrogen dioxide, besides being able to detect this analyte in the range 100–1000 ppb in agreement with the requirements of the project.

3 Test Platform with NO_2 Gas Sensors

Four devices, prepared starting from pristine and functionalized graphene, were sent to the CEA for the connection with an electronic board, specifically designed for sensor data acquisition in real time. The platform is compatible with different kinds of sensors, i.e. able to monitor both vital parameter (activity, core body temperature, electrolytes and biomarkers) and the chemical composition of the ambient air (NO_x, CO_x, particles); data were directly sent by Bluetooth on smartphones. Table 1 summarizes the main features of the prepared devices.

The sensors were plugged onto the sensor platform that converts through an ADC Voltage Divider Bridge the analog electric signal into a measurable signal, as shown in Fig. 2.

Table 2 displays the main electrical parameters measured after the connection to the platform. The resistance values, both measured by a multimeter and by the plat-

Table 1 Summary of the basic resistance values of the sensors produced by ENEA and the corresponding sensitivity towards NO_2

	Sample name	R (kΩ)	Sensitivity to NO_2
Pristine graphene	ENEA 1	0.46	37% @ 300 ppb
Pristine graphene	ENEA 2	0.4	31% @ 1 ppm
Pristine graphene	ENEA 3	1.9	23% @ 1 ppm
ZnO NP decorated graphene	ENEA 4	88	50% @ 1 ppm

Fig. 2 NO_2 sensors (ENEA) tests

Table 2 Summary of the main electrical parameter checked after the connection to the Leti-CEA platform

	Multimeter measures (Ω)	Platform measures (Ω)	Error (%)	Value converted by the ADC (V)
ENEA 2	593	598	0.8	145
ENEA 3	1984	2009	1.26	477

form, are in agreement with an error of about 1%, thus indicating that the connection to the platform did not introduce any contact resistance.

After these characterizations, devices ENEA 3 and ENEA 4, connected to the CEA platform were tested into ENEA sensor test chamber with a measurement protocol that includes 20 min in an inert environment, 10 min of exposure to the analyte and the restoration phase in an inert environment for 20 min. As can be seen in Fig. 3,

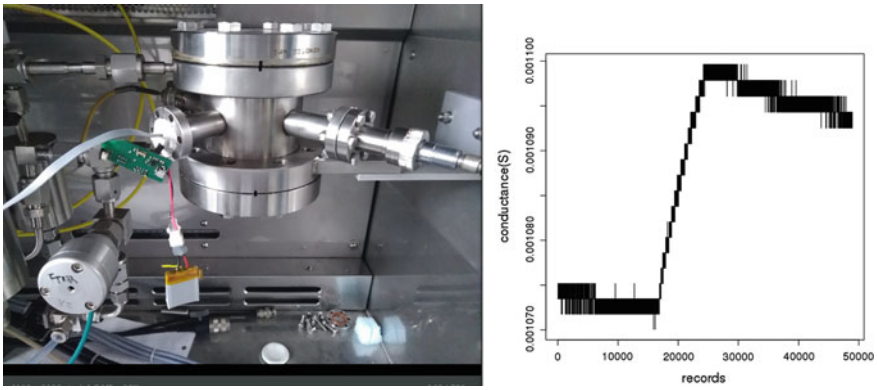

Fig. 3 Pristine graphene-based sensor, named ENEA3, installed on LETI board, exposed to 300 ppb of NO_2 for 10 min

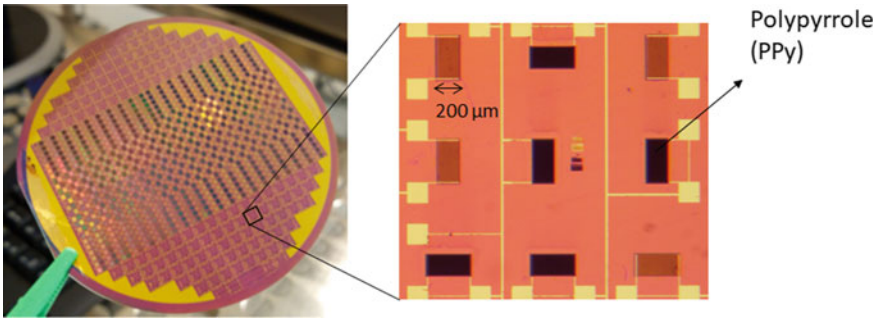

Fig. 4 Example of a multi-pixel platform; each transducer consuming less than 20 µW in continuous operation

ENEA3 device installed on LETI board and exposed to 300 ppb NO_2, exhibits a variation of 3%, so demonstrating that the platform is able to follow and visualize in real time on a Smartphone the signal variation consequent to the exposure to such analyte.

These preliminary tests allowed identifying some parameters on which to optimize the sensor devices. In particular, for an optimal Analog to Digital Conversion, the coupling of the sensor device resistance with that of the Voltage Divider Bridge (67 kΩ) should be realized so as those values result as close as possible. According to this, the further development of sensing devices will be carried out in such a way as to obtain a basic resistance contained in the identified range, in order to work with the maximum ADC input dynamic voltage range, that will allow a limit of NO_2 detection as low as 50 ppb.

4 Sensing Material Deposition on UCL Microarrays

The same preparations based on bare and ZnO-functionalized graphene were dispensed by drop casting on a multi-pixel resistive CMOS-compatible platform functionalizable with gas sensing materials operating at room temperature, specially designed by UCL looking at ultra-low-power low-cost environmental monitoring. An example of platform is depicted in Fig. 4.

Besides, a communication platform has also been implemented for Internet of Things (IoT) applications through LoRaWAN protocol on dedicated networks. Data integration and visualization are performed in partnership with Opinum S.A. company. Figure 5 shows the dies sent to the ENEA lab for the sensitive materials deposition. The microarrays are of two types: 2×2 pixel^2 and 3×3 pixel^2, the size of sensitive surfaces goes down to 300×200 μm^2. This should highlight miniaturization capabilities towards a versatile low-cost multi-gas sensing microsystem.

In this first phase we tested the drop casting deposition on 2×2 structures, by dispensing the materials onto microstructures by using a microsyringe. The 3×3 arrays were instead put aside and destined to inkjet deposition to be carried out in a second phase. Figure 6 displays a photo of the 2×2 microarrays on which the sensing materials were dispensed. The resistance values of the devices resulted to fall into the kΩ range, therefore suitable for the subsequent bonding and encapsulation.

The main critical issues emerged during these tests indicate the need to further refined the deposition technique, in order to avoid both the overlapping of material between two adjacent devices and also the contact between the microsyringe tip and the substrate, which can cause scratches on the interdigitated structure. We are confident that all the abovementioned issues can be avoid on 3×3 array kept for inkjet deposition; indeed, such approach allows to deposit the sensing material based-ink in controlled way also avoiding contact between the dispensing medium and the sample surface, thus resulting totally safe.

5 Conclusions

In this document we presented the first steps of the CONVERGENCE project, which involves ENEA group together with CEA (Commissariat à l'Energie Atomique, France) and UCL (Université catholique de Louvain, Belgium).

The interfacing of graphene-based gas sensors with LETI board and the subsequent exposure to 300 ppb NO_2, demonstrated the ability of the platform to follow and visualize in real time the sensing signal; an adequate sizing of the coupling of the sensor device resistance with that of the Voltage Divider Bridge will allow a limit of NO_2 detection as low as 50 ppb.

Deposition of bare and ZnO-functionalized graphene on a multi-pixel resistive CMOS-compatible platform has produced devices with electrical resistance values suitable for the subsequent bonding and encapsulation; some weaknesses emerged

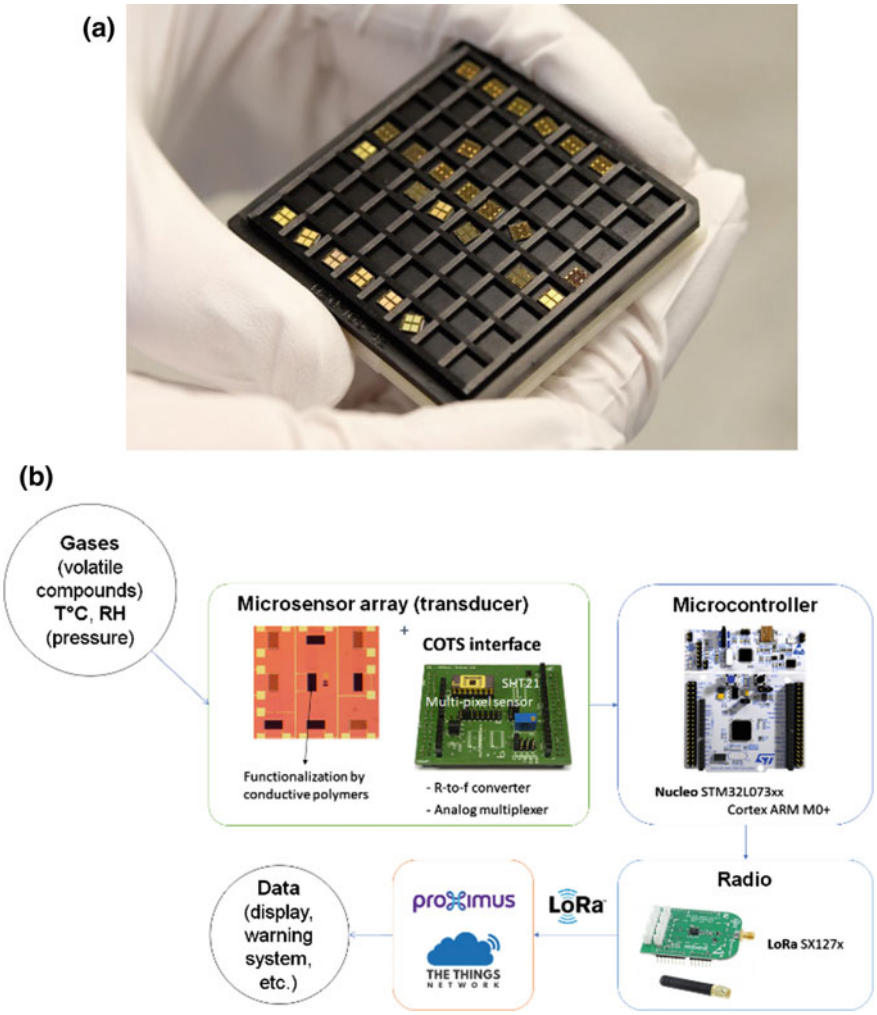

Fig. 5 **a** Multi-pixel array platforms based on interdigitated microelectrodes sent to ENEA for pristine graphene and GZnO deposition and further characterizations after encapsulation and bonding. **b** Full IoT system implementation

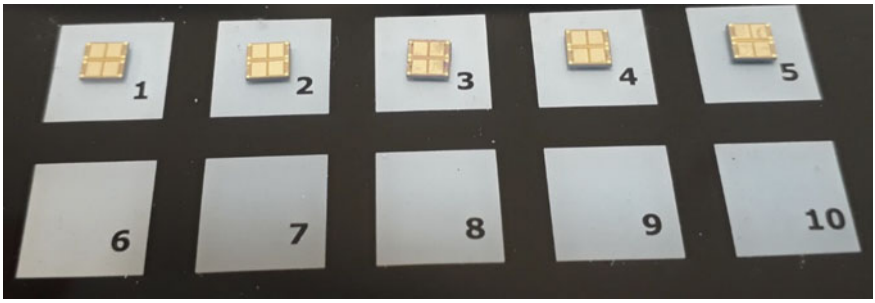

Fig. 6 Photograph of the bare and functionalized graphene-based devices realized by drop casting on UCL microarrays

during these tests, mainly related to the deposition technique, such as overlapping of the sensing film between two adjacent devices and scratches on the interdigitated structure. Such drawbacks will be overcome by utilizing inkjet printing deposition.

Acknowledgements CONVERGENCE is funded by the Flag ERA (ERANET—JTC2016).

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