Lecture Notes in Electrical Engineering 539

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Corrado Di Natale · Vittorio Ferrari
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Sensors

Proceedings of the Fourth National Conference on Sensors, February 21–23, 2018, Catania, Italy

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Preface

This book gathers scientific contributions presented at the 4th National Conference on Sensors held in Catania, Italy from 21 to 23 February 2018. The conference has been organized by a partnership of the major scientific societies and associations involved in the research area of sensors, the Italian Society of Chemistry (SCI), the Italian Association of Electric and Electronic Measures (GMEE), the Italian Association of Ambient Assisted Living (AITAAL), the Italian Society of Optics and Photonics (SIOF), the Italian Association of Sensors and Microsystems (AISEM), the Italian Society of Pure and Applied Biophysics (SIBPA), the Italian Association of Photobiology (SIFB), the Association Italian Group of Electronics (GE), and the Association NanoItaly.

The fourth edition of the conference has confirmed a large participation with approximately 70 oral presentations, 80 poster presentations, and over 150 delegates. The driving idea of the first conference, to gather scientists having different expertise and with different cultural backgrounds, dealing with all the different aspects of sensors, has proved to be indeed successful again.

In this perspective, the book represents an invaluable and up-to-the-minute tool, providing an essential overview of recent findings, strategies, and new directions in the area of sensor research. Further, it addresses various aspects based on the development of new chemical, physical, or biological sensors, assembling and

characterization, signal treatment, and data handling. Lastly, the book applies electrochemical, optical, and other detection strategies to the relevant issues in the food and clinical environmental areas, as well as industry-oriented applications.

Catania, Italy — Bruno Andò
Florence, Italy — Francesco Baldini
Rome, Italy — Corrado Di Natale
Brescia, Italy — Vittorio Ferrari
Catania, Italy — Vincenzo Marletta
Florence, Italy — Giovanna Marrazza
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Part I
Chemical Sensors

Low Temperature NO_2 Sensor Based on $YCoO_3$ and TiO_2 Nanoparticle Composites

Tommaso Addabbo, Ada Fort, Marco Mugnaini and Valerio Vignoli

Abstract Chemical sensors based on metal oxides have been widely explored and used in the literature and have found different application fields as a function of their operating characteristics like selectivity, sensitivity, stability over time etc. Recently, some papers started to diffuse the idea that innovative chemical sensors could be obtained using two different metal oxides combined together providing enhanced sensing capabilities. In this paper the authors propose a new sensor based on perovskite support modified by a TiO_2 based compound in order to test enhanced sensing performance. Moreover, the present work aims to show that nanocomposites obtained introducing in a matrix of a given metal oxide a second nano-structured metal oxide, which can act either as a catalyst or as a structure modifier, can provide improved sensitivity, selectivity and stability.

Keywords Chemical sensors · Metal oxide sensors · Hetero-junctions

1 Introduction

Recently many research works have shown that in general all types of nanocomposites are very promising for the development of resistive gas sensors [1]. It was established that the surface-related properties important for gas sensor applications

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such as electronic, catalytic, mechanical, and chemical ones can be highly modified and tuned to the specific applications by combining different nano-structured materials [1–3]. The most traditional composites used in gas sensors are those obtained by the addition of noble metals to metal oxide matrices, but recently also many other composites were proposed and tested, such as films consisting of polymers mixed with metals or metal oxides, or carbon nanotubes mixed with polymers, or again composites based on fullerenes and graphene, etc.

In this context, composites based on the combination of two different nano-structured metal oxides, Me_IO and $Me_{II}O$, have proven to be extremely interesting. Nanocomposites obtained introducing in a matrix of Me_IO a nano-structured $Me_{II}O$, which can act either as a catalyst or as a structure modifier, can provide improved sensitivity, selectivity and stability. Metal Oxide-Metal Oxide structures can be implemented in several ways. They can be created during the process of either synthesis or deposition of initial material, or can be formed by various layer by layer techniques, or alternatively they can be generated by mixing already synthetized materials in certain proportions.

Anyhow it must be underlined that both in thin and thick film deposition, controlling the chemical compositions, surface morphology microstructure and phase state is still a challenge since, in general, the sensing characteristic are controlled independently by three factors (which are Receptor function, Transducer function and Utility factor [1]) which describe and participate in the generation of the sensor signature. The Receptor function is strictly linked to the material redox properties, to the stochiometry, and to the adsorption/desorption parameters. The Transducer function mainly depends on the carrier mobility, concentration and on the grain size, whereas the Utility factor is linked to the film thickness and geometrical factors [1–3]. Therefore any sensor has its peculiar characteristic depending on the combination of these factors which are really difficult to be controlled during the fabrication process.

2 Sensors and Characterization

2.1 Sensor Preparation

In this paper we propose a NO_2 sensor based on a composite obtained exploiting an already-prepared metal oxide matrix of $YCoO_3$ pervoskite. Perovskite powders were prepared by means of a sol-gel method, described in detail in [4], both in stoichiometric form and in Pd doped and defective versions. The powders were mixed to organic vehicles to prepare a paste which was screen printed on Alumina substrates across two electrodes. A transparent n-TiO_2 coating produced by Italvernici

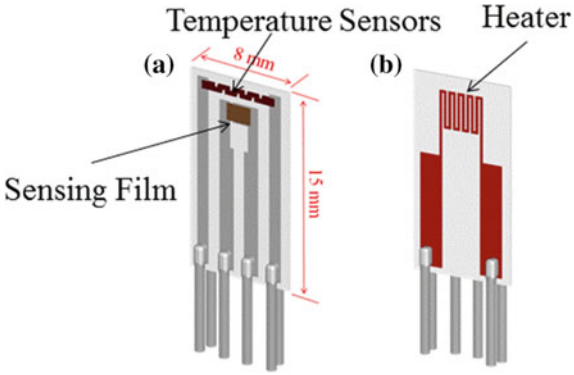

Fig. 1 Chemical sensor layout. On side (**a**) the sensing film and the temperature sensors are designed and implemented through screen printing technique. On the (**b**) side the heater is realized by means of the same technique

(ITALVERNICI-FELCE150) [5] has been used for wet impregnation of the printed layer by drop casting (2 μL doses) using a micropipette; the as-obtained film was heated at 320 °C for 24 h. The n-TiO_2 coating used in this study is based on crystalline anatase (nanoparticle dimensions in the range 25–55 nm) diluted in water with a concentration of 32×10^{-4} mol/L to get a transparent paint with 2.0 cPs viscosity. The obtained nano-composite consists of highly dispersed TiO_2 in the frame-work of the perovskite matrix. The sensing support is a screen-printed thick-film alumina circuit hosting the sensing layer and a temperature sensor on one side and a heater on the other side (Fig. 1).

2.2 Sensor Characterization

The sensors were characterized by means of a system which allows for accurately controlling the temperature of each sensor, as well as the gas mixture flow and composition, also in terms of humidity, as shown in Fig. 2 and described in [4–8].

In detail, with reference to Fig. 2, the system exploits gas reservoirs which feed, by means of a flowmeter bench, a measurement chamber equipped with 8 chemical sensors. The chamber is maintained at a constant temperature in an incubator. The front end electronic boards (one for each sensor, housed inside the measurement chamber) are connected to a NI PXI rack where a host processor board and ADC and DAC boards are used to control the measurement process and to acquire the measurement data. A personal computer is used to set the measurement parameters and to process and display the measurement data.

The sensors were tested under a constant flow (200 mL/min) of mixtures of NO_2 with a carrier gas that was N_2 or air, humid and dry.

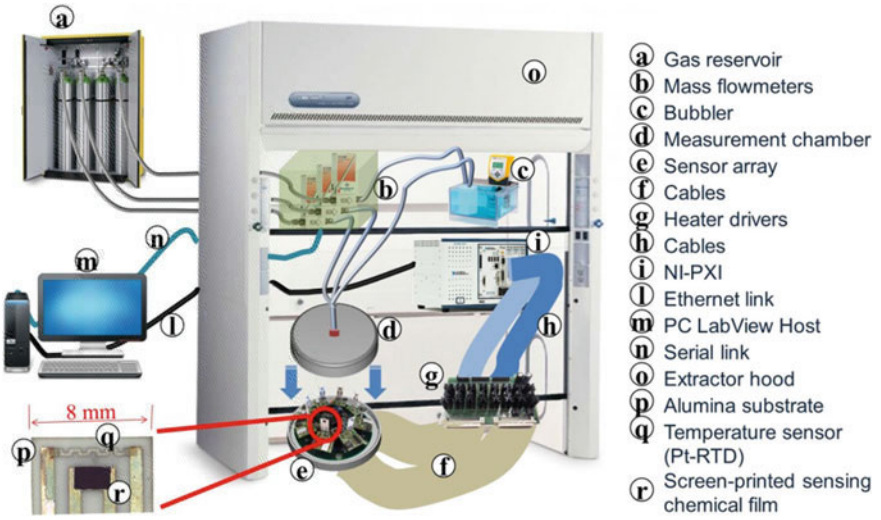

Fig. 2 Chemical sensing system used for characterization

Figures 3 and 4 show the responses to NO_2 of sensors obtained with different $YCoO_3$ based materials, before and after the impregnation with n-TiO_2, as a function of temperature and as a function of time, respectively.

The response is defined as $(R - R_0)/R_0$, where R_0 is the baseline resistance of each individual sensors measured at the same temperature in the carrier gas (nitrogen or air), whereas R is the value of the sensor resistance after 4 min of exposition to the test mixture.

The results presented in this paper show that the introduction of TiO_2 (n-type semiconductor) in the matrix of $YCoO_3$ (p-type) highly improves the sensitivity toward NO_2 at low temperature (in fact the sensors could be used also at room temperature, as shown in Fig. 5).

The insertion of TiO_2 nano-particles on the surface of the $YCoO_3$ larger grains produced hetero-junctions (see Fig. 6), which due to microstructure of the layer contribute only marginally to the electronic conduction in the sensing film, which is instead mainly determined by the behavior of the homo-junctions at the $YCoO_3$ grains boundaries. Nevertheless, the large effect observed could be explained both by the enhancement of the depleted region at the surface of the $YCoO_3$ grains, which can both modify the height of the Schottky barriers at the homo-junctions and favor the adsorption of oxidizing gases, and by the large reactivity of TiO_2 toward NO_2 also at low temperature.

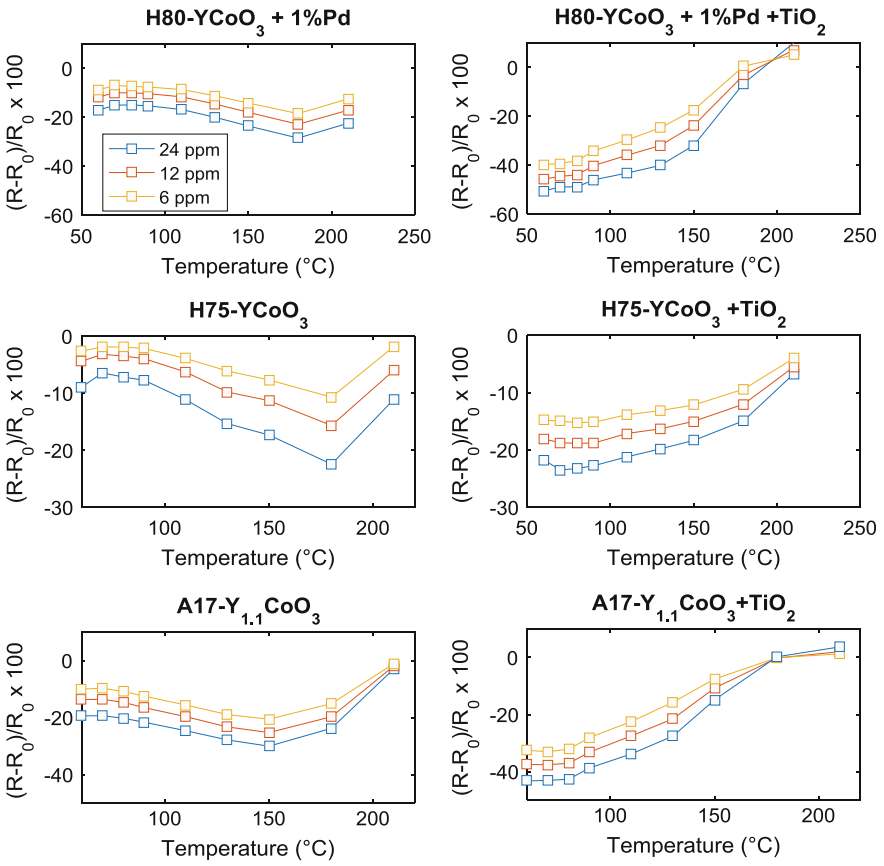

Fig. 3 Responses of 3 different materials based on $YCoO_3$ to NO_2 as a function of working temperature for different NO_2 concentrations (as per legend). Leftmost plots: without TiO_2. Rightmost plots: with TiO_2 nanoparticles. The carrier gas is nitrogen, the flow is 200 mL/min. The values of R are obtained after 4 min of exposition to the target mixtures

3 Conclusions

In this paper the authors presented a new sensor obtained by means of an hetero-junction based on both a perovskite material and TiO_2. The introduction of TiO_2 (n-type semiconductor) in the matrix of $YCoO_3$ (p-type) highly improves the sensitivity toward NO_2 at low temperatures. The insertion of TiO_2 nano-particles on the surface of the $YCoO_3$ larger grains produced hetero-junctions, which slightly modify the material conductive properties. Nevertheless, the electronic conduction in the sensing film is still mainly determined by the behavior of the homo-junctions at the $YCoO_3$ grains boundaries. As a matter of fact, it seems that the depletion

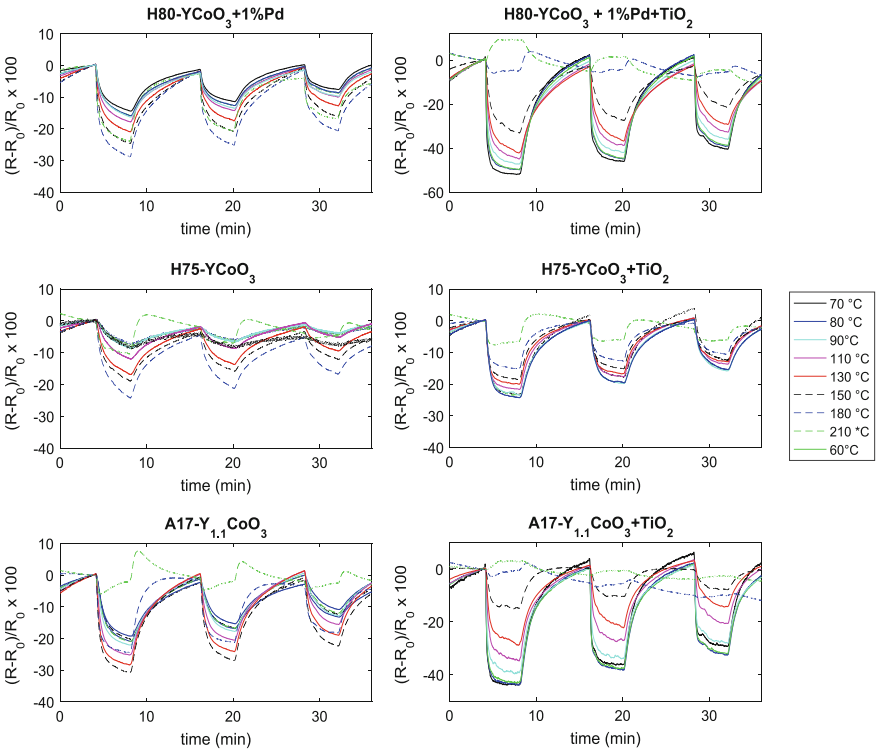

Fig. 4 Transient responses of 3 different materials based on $YCoO_3$ to NO_2 as a function of time at different temperature (as per legend). The carrier gas is nitrogen, the flow is mL/min with the following protocol: 4 min N_2, 4 min N_2 + 24 ppm NO_2, 8 min N_2, 4 min N_2 + 12 ppm NO_2, 8 min N_2, 4 min N_2 + 6 ppm NO_2, 4 min N_2

region of newly induced junctions is affected by the TiO_2 nano-particles favoring the adsorption of oxidizing gases.

The proposed sensors seem interesting in all the possible applications where temperature may play an important role in terms of power consumption requirement due to the fact that exploitable sensor responses can be obtained even starting from ambient temperature.

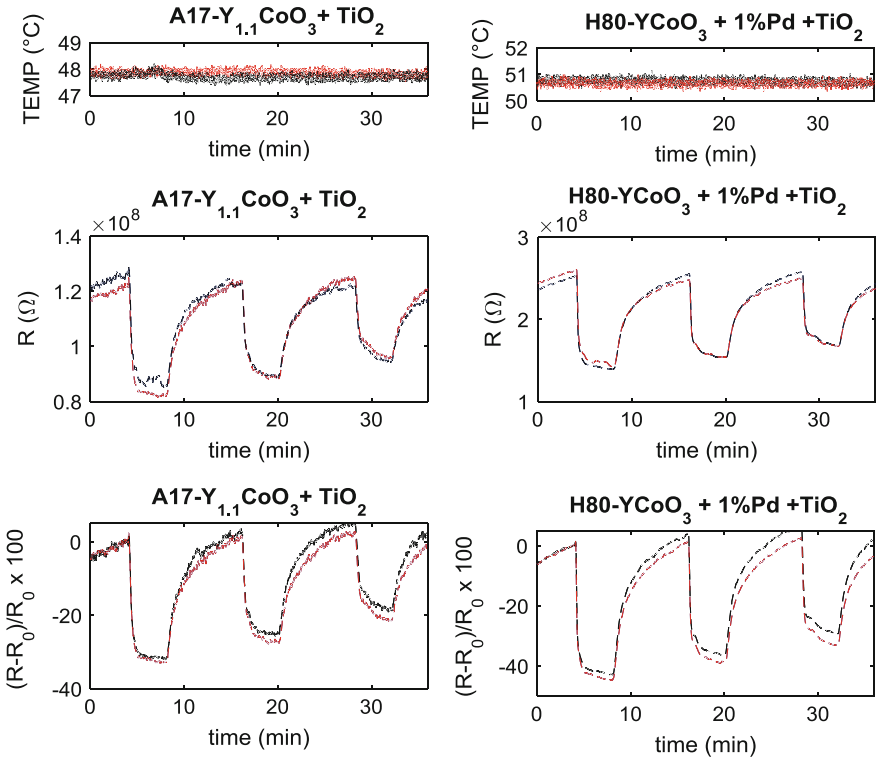

Fig. 5 Transient responses of 3 different materials based on $YCoO_3$ to NO_2 as a function of time. The heater wasn't driven

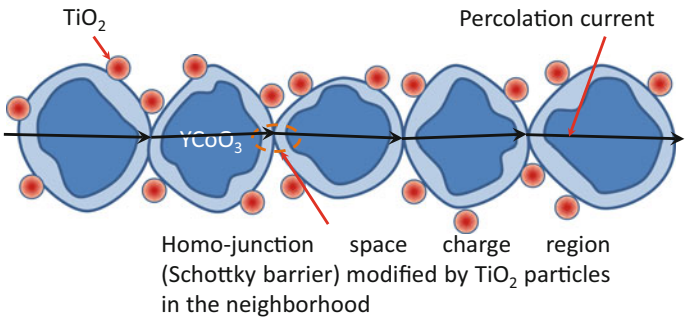

Fig. 6 Schematic of the structure and of the conduction mechanism of the proposed composite

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Effect of Humidity on the Hydrogen Sensing in Graphene Based Devices

Brigida Alfano, Ettore Massera, Tiziana Polichetti, Maria Lucia Miglietta and Girolamo Di Francia

Abstract In this work, we investigate the effect of humidity variations on the sensing performance of Pd-graphene (GR) based devices. Palladium nanoparticles are directly synthetized onto GR sheets by microwave irradiation; the optimal palladium coverage results into a sensitive and fast hydrogen device. The dynamic conductance changes exposed to different hydrogen concentrations from 2.5 to 0.2% are displayed at room temperature, using humidified air as carrier gas at different Relative Humidity (RH) levels. The results show how the sensing curves in low humidity conditions have higher sensitivity with respect to humid environment. On the other hand, dry conditions negatively affect the sensing layer stability over time while humid conditions preserve the material.

Keywords Graphene · Metal decoration · Hydrogen detection

1 Introduction

Graphene is a two-dimensional material made of carbon atoms, so far called "wonder material" for its exceptional physical characteristics. Since its discovery in 2004, researchers are enthusiastically studying graphene to exploit its outstanding properties in numerous applications [1].

Graphene could represent a powerful sensing material to design smaller and lighter sensor respect to conventional ones. Moreover, employing its characteristic electronic structure, the device based on graphene could be able to detect rapidly a single molecule also at room temperature [2].

Pristine graphene is particularly sensitive towards nitrogen dioxide [3, 4].

In this regard, the functionalization with metal and metal oxide nanoparticles proves to be an effective way to extend the range of analytes to which the material is sensitive [5–9].

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The possibility of functionalization further improves the prospects of graphene-based electronics for a real industrial application. In this scenario, the effect of metal nanoparticles decoration onto graphene surface has been addressed in our latest works [10]. We have fabricated a chemiresistor based on graphene, functionalized with palladium nanoparticles, highly sensitive towards hydrogen gas [11].

Since the functionalization has a direct effect on sensing behavior, it is crucial to determine the optimum coverage surface to obtain the most performing device [12].

The fabricated device follows linearly the variations in hydrogen concentration, showing repeatable responses when exposed to cyclic tests.

Herein, a further investigation about the dynamic behavior of sensing device is displayed, with the aim to approach the real world operating conditions. First of all, the effect of humidity was considered and then the history of device.

1.1 Material Preparation

As reported in our previous work [13], pristine graphene was synthesized by Liquid Phase Exfoliation (LPE) method: natural graphite flakes, dispersed in a hydro-alcoholic solution, were exfoliated by means of ultrasound treatment. The surface of pristine graphene was decorated according to the process described in our previous works [11, 12].

1.2 Material Characterization

A drop of the freshly-sonicated dispersions of graphene decorated with Pd nanoparticles (PdNPs) was casted on n-doped Silicon substrate and dried on hot plate for Scanning Electron Microscopy characterization.

The graphene flakes, with an average lateral size of 300 nm, are randomly overlapped (Fig. 1). These are constituted by few layers, as evidenced in Raman spectroscopy data reported in our previous works [11, 12]. In the SEM image (Fig. 1), PdNPs appear as bright spots all over the graphene surface with average size of 30–40 nm.

1.3 Sensing Characterization

For the electrical and sensing characterization, few microliters of suspension were drop casted onto rough alumina transducers with five pairs of gold interdigitated electrodes (fingers 350 μm wide, 4650 μm long and 350 μm spaced).

For each device, the achievement of the ohmic contact between GR-PdNPs films and gold electrodes was proven by the linear response of I–V measurements (Fig. 2c).

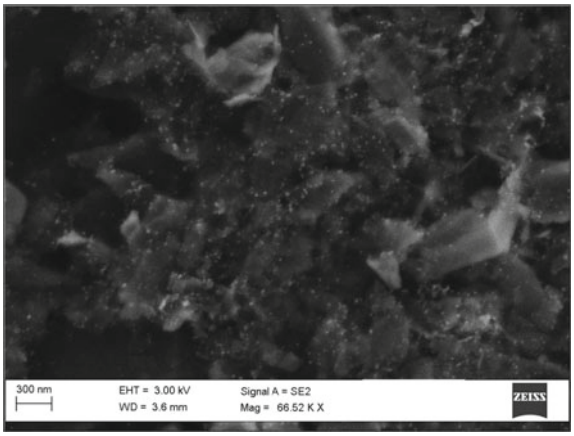

Fig. 1 SEM image Pd nanoparticles onto graphene sheets

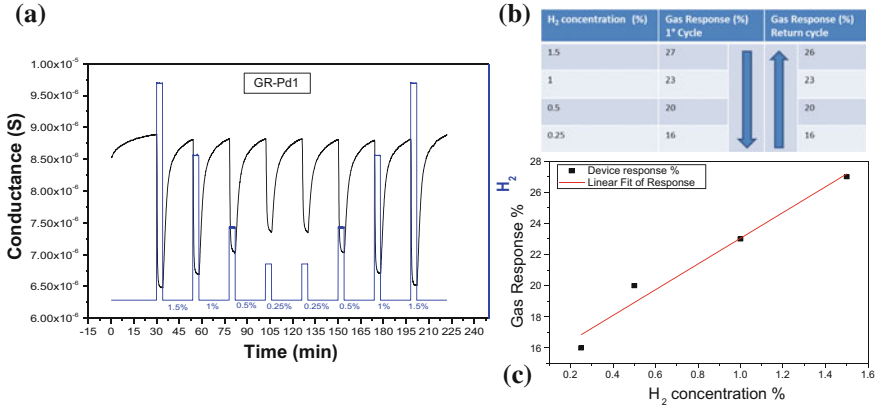

Fig. 2 **a** The dynamic conductance changes of GR-Pd device exposed to different hydrogen concentrations from 1.5 to 0.25% and the return cycle; **b** gas responses according to H_2 concentration for the first cycle and for return cycle; **c** IV characteristic

The as-fabricated devices were characterized by recording their conductance change when exposed to hydrogen gas. In particular, we have investigated the performances of the devices in terms of the percent conductance change consequent to a gas exposure, in absolute value, which we regard as gas response (Eq. 1).

$$\text{Gas Response}\,(\%) = \frac{|G_{\max} - G_0|}{G_0} * 100 \tag{1}$$

where G_0 and G_{max} are the conductances of the devices before and after the exposure to a gas, respectively.

The device is able to follow the changes of hydrogen gas concentration from 0.25 to 1.5% (the specific concentrations are labeled under each peak in Fig. 2a) in humid atmosphere (RH 50%). By considering the responses recorded during the measurement cycle, it can be observed as the response values at the same hydrogen concentration are identical within the error of measurement (±0.2%).

This chemiresistor presents interesting sensing properties: in controlled environment the device follows linearly the hydrogen concentration and the sensing responses are repeatable. It is worth noting that these performances have been realized working at room temperature. However, for the application in a real environment, it is crucial to know how the device behaves when external conditions change. In actual environment, the most important interferent for any sensing device, even for high-temperature operating devices, is water. As so, in the first step, the relative humidity (RH) was changed in the test chamber in the range 0–50% RH.

Figure 3 shows the dynamic conductance changes of the device exposed to different hydrogen concentrations at room temperature under different humidity conditions, namely at Relative Humidity (RH) levels of 50, 10 and 0%. In low humidity conditions, from 0% RH to 10% RH, upon hydrogen exposure and after the sensing phase, the conductance signal shows a continuous drift towards higher values (Fig. 3b, c), while at 50% RH, the conductance signal drops slightly after every sensing phase (Fig. 3a). Basically, in low humidity environment an *over-recovery* of the sensing signal is observed while the reverse occurs in medium to high humidity environments.

The desorption phase of hydrogen from Pd structures involves the interaction of oxygen with the palladium hydride (formed during the exposure) with the restoring of Pd and formation of a water molecule [14, 15]. As can be seen in Fig. 3a, in humid environment this process does not lead to a complete reaction and it is likely that some H_2 remains trapped into the Pd structures so determining its volumetric expansion also concurring to the lower conductance values. On the contrary, it can be hypothesized that in low humidity conditions, where the reaction between oxygen and adsorbed hydrogen is favored, even the hydrogen previously trapped reacts with oxygen. This mechanism could be at the basis of the *over-recovery* phenomenon observed in Fig. 3b, c).

These results suggest that environmental conditions can affect sensing performances, and those performances may degrade more or less quickly based on the "history" of the device. This is clear if we refer to Fig. 3d, where the sensitivity curves recorded at different humidity levels and the subsequent measurement cycles in dry conditions are summarized. As can be seen, the sensitivity in dry environment appears higher, but the curves also lose the linearity as the overall exposure of device to hydrogen increases. This can be ascribed to the aforementioned volumetric expansion of the Pd nanoparticles, which is at the basis of the well-known issue of the metallic embrittlement by hydrogen [16]. Of course, this modification of the material causes a parallel loss of sensing properties.

In other words, the operation of the device in real environmental conditions, characterized by the constant presence of humidity, preserves this kind of sensitive film from a fast deterioration even though this leads to a decrease in sensitivity.

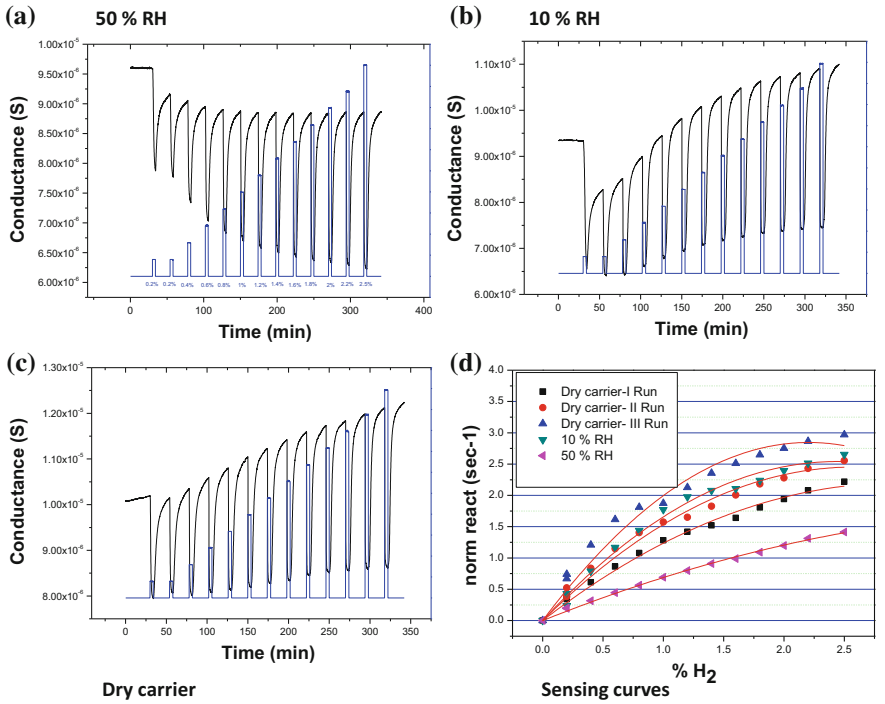

Fig. 3 The dynamic conductance change of device exposed to different hydrogen concentrations from 2.5 to 0.2% changing RH levels **a** 50% RH, **b** 10% RH, **c** Dry carrier, at RT; **d** Humidity effect on sensing curves. To overcome the uncompleted recovery and the changing baseline, we have used the correlation between the maximum rate of the relative response and hydrogen concentration (reactivity), method discussed in our previous work [4]

2 Conclusions

In this work, we have investigated the effect of humidity variations on the sensing performance of Pd-graphene (GR) based devices.

The experiments have shown that exists a loss of response linearity at high concentrations of hydrogen as a consequence of cyclic H_2 exposures, which cause morphological changes. Tests in environmental conditions (50% RH) have shown that despite a smaller sensitivity with respect to dry conditions, the presence of humidity preserves the sensing film.

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