DOI 10.5162/EUROSENSORS2025/W7.1.4

Ultrafast Recovery and Humidity Effect in a MoS_2-ZnO functionalized CNTs Array driven as an e-nose

Michele Galvani[1], Luigi Sangaletti[1]
[1] Surface Science and Spectroscopy Lab at I-Lamp, Department of Mathematics and Physics, Via della Garzetta 48, 25133 Brescia, Italy.

Summary:
Gas sensors are essential in various fields, and high chemical selectivity and fast response/recovery times are crucially important. Chemiresistors based on nanomaterials are still a central sensors category due to ease of fabrication, which allows for an easy prototyping of novel architecture, especially when sensor arrays are operated as e-noses. Here, we present an array of fast and highly selective gas sensors using CNTs layers decorated with ZnO and MoS_2. The sensors exhibit strong NH_3 selectivity, with recovery times below 10 seconds. Lastly, the array can be operated as an electronic nose, successfully discriminating the different target gas molecules using both scatter plots and PCA analysis.

Keywords: chemiresistors, carbon nanotubes, response-recovery times, electronic nose, PCA.

Background and Motivation

Gas sensors represent an extremely active field of research. New devices play a fundamental role in various sectors, including industry (food and beverage, automotive, etc.) and air quality monitoring. Sensors need to be chemically selective, meaning they should react only to the chosen target gases, and fast, then capable of responding and recovering from gas exposure quickly enough to be suitable for industrial applications.

There are several types of gas sensors, each based on different working principles. Among them, chemiresistors still represent an opportunity to develop and prototype novel architectures, due to their low production cost, compact size, and ease of implementation. Additionally, the use of machine learning algorithms and approaches for data analysis have shown to be able to expand the sensors performances when used in e-noses.

Regarding nanostructured carbon based chemiresistors, the fastest ones, in terms of response and recovery time, have t_{res} and t_{rec} of the order of 5-10 seconds [1].

Within this context, an array of ultrafast and highly selective gas sensors based on zinc oxide nanoparticles (ZnO NPs), and molybdenum disulfide nanoflakes (MoS_2 NFs)-functionalized carbon nanotubes (CNTs) is presented. Both the functionalization strategies are widely used in chemiresistors and are often combined with nanostructured carbon to achieve fast and responsive NH_3 sensors (see e.g. [2] and [3]).

Materials and methods

Four samples were prepared: pristine CNTs, (without functionalization), CNTs decorated with MoS_2 NFs (CNT + MoS_2), with ZnO NPs (CNT + ZnO), and with a combination of both (CNT + MoS_2 + ZnO). The solutions, along with the functionalizations, have been dropcasted onto 13.4x7 mm^2 interdigitated electrodes (IDEs), composed of an insulating alumina substrate and a conducting silver pathway. The sensors were then characterized using an inVia™ Raman microscope, to check also possible doping effects induced by the functionalization.

All samples were tested in a chemiresistor configuration, using a custom-developed control setup, consisting of an electronic breadboard for resistance measurements and a dedicated LabView procedure. The sensors were exposed to various contaminants, particularly ammonia and water. The resulting responses were then analyzed using appropriate Python procedures to assess the array's discriminating capabilities.

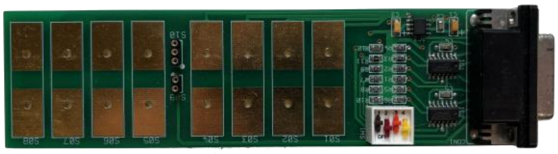

Fig. 1. Chemiresistors controlling breadboard.

Results

All four samples exhibit different responses to ammonia and water. The results are reproducible. Figure 2 shows their dynamical responses while exposed to different ammonia concentrations and RH variations. RH and NH_3 were measured with properly calibrated commercial sensors. RH baseline value was set at 70%.

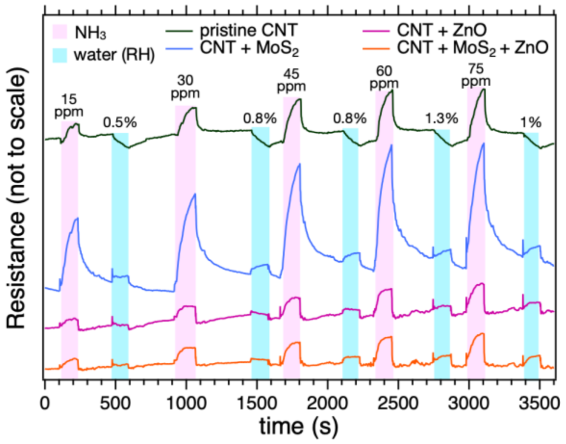

Fig. 2. Chemiresistors dynamical responses to an ammonia-water concentration ramp.

Response and recovery times have been calculated. Notably, despite the sensors operating in a static regime [4], the recovery time remains well below 10 seconds. The t_{res} and t_{rec} values for ammonia and water exposures, measured for the CNT + ZnO sensor, are presented in Figure 3.

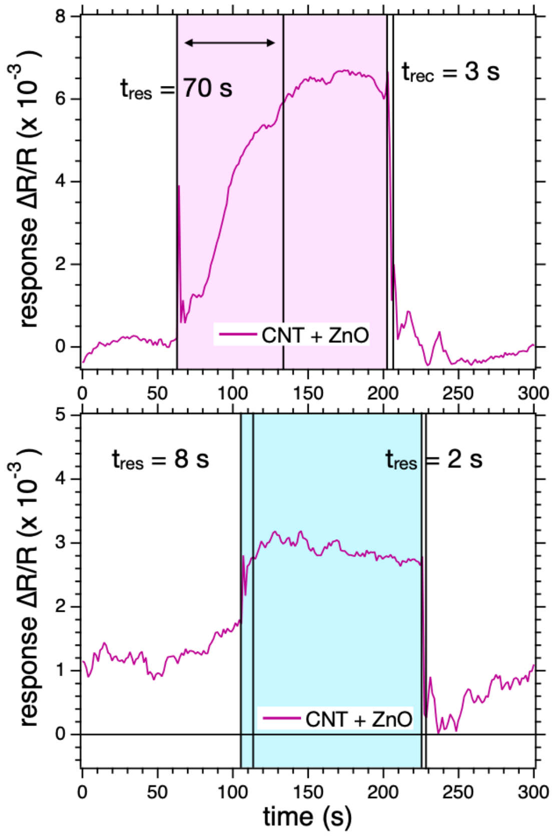

Fig. 3. CNT + ZnO sensor velocity to ammonia (top panel) and water (bottom panel).

Additionally, the sensor array was tested with other target gases, including some volatile organic compounds (VOCs), such as acetone, ethanol, and isopropyl alcohol (IPA), and nitrogen dioxide. We observed that different contaminants produce distinct response patterns in the array, enabling their complete discrimination. Responses scatter plots and PCA analysis are presented in Figure 4. It is possible to notice that with both techniques a complete separation of the target gas is obtained. However, PCA offers a better clustering of the points, due to the collective contribution of all sensors. Clustering algorithms, such as DBSCAN, and indicators like silhouette score were be used to quantify the mentioned results.

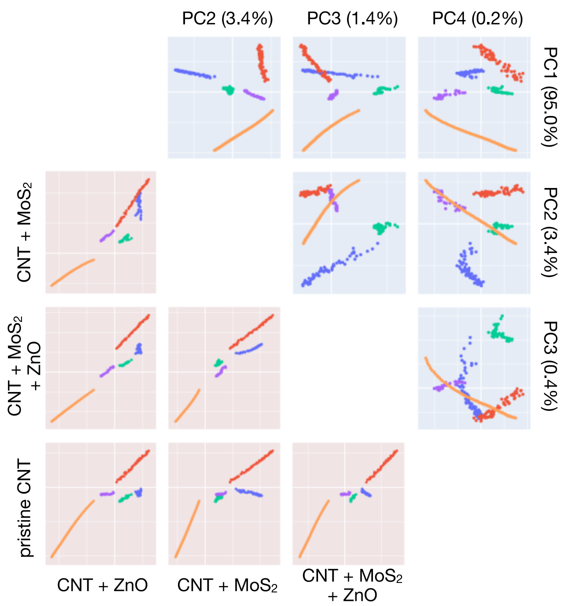

Fig. 4. Responses scatter plot and PCA.

References

[1] M. Galvani, S. Freddi, L. Sangaletti, Disclosing fast detection opportunities with nanostructured chemiresistor gas sensors based on metal oxides, carbon, and transition metal dichalcogenides, *Sensors* 24.2, 584 (2024); doi: https://doi.org/10.3390/s24020584

[2] M. Abniel, et al. Sensitive and reversible ammonia gas sensor based on single-walled carbon nanotubes, *Chemosensors* 11.4, 247 (2023); doi: https://doi.org/10.3390/chemosensors11040247

[3] M. Morsy, et al. Portable and battery operated ammonia gas sensor based on CNTs/rGO/ZnO nanocomposite, *Journal of Electronic Materials* 48, 7328-7335 (2019); doi: https://doi.org/10.1007/s11664-019-07550-7

[4] A. Ponzoni, A statistical analysis of response and recovery times: the case of ethanol chemiresistors based on pure SnO2, *Sensors* 22.17, 6346 (2022); doi: https://doi.org/10.3390/s22176346