chemistry proceedings

Proceedings

Morphological Effects in SnO_2 Chemiresistors for Ethanol Detection: a Systematic Statistical Analysis of Results Published in the Last 5 Years †

Andrea Ponzoni

National Institute of Optics of the National Research Council (CNR-INO), unit of Brescia, 25123 Brescia, Italy; andrea.ponzoni@ino.cnr.it

† Presented at the 1st International Electronic Conference on Chemical Sensors and Analytical Chemistry, 01—15 July 2021 ; Available online: https://csac2021.sciforum.net/.

Abstract: SnO_2 is one of the most studied materials in gas sensing. Among the many strategies adopted to optimize its sensing properties, the fine tuning of the morphology in nanoparticles, nanowires, nanosheets and their eventual hierarchical organization has become an active field of research. In this work, results published in literature in the last five years are systematically analyzed focusing on response intensities recorded with chemiresistors based on pure SnO_2 for ethanol detection in dry air. Results indicate that no morphology clearly outperforms others, while a few individual sensors emerge as remarkable outliers with respect to the whole dataset.

Keywords: Chemiresistors; SnO_2; Ethanol; Nanoparticles; Nanorods; Nanosheets

Citation: Ponzoni, A. Morphological effects in SnO2 chemiresistors for ethanol detection: a systematic statistical analysis of results published in the last 5 years. *Chem. Proc.* **2021**, *3*, x. https://doi.org/10.3390/xxxxx

Published: 1 July 2021

1. Introduction

Chemiresistors based on semiconducting metal oxides are among the most popular gas sensing devices, their success arising from their high sensitivity to a broad range of chemicals, reduced size and power consumption, suitability for mass production at relatively reduced costs. To optimize the sensing layer, the fine control of the morphology, both at the level of individual nanostructures and at the level of their hierarchical assembly, has been reported as very effective [1,2].

In this work, with the aim to have a more general and reliable picture of the state of the art, results published in the literature in the last five years are systematically analyzed focusing on response intensities recorded with chemiresistors based on pure SnO_2 for ethanol detection in dry air, as case example. In particular, we chose to focus on SnO_2 because it is the most studied material among semiconducting metal oxides. Similarly, we chose ethanol as target gas because it is widely used as test gas for the development of innovative materials (morphologies) and it is a key component in many applications [3].

2. Materials and Methods

This work considers the responses to ethanol reported for chemiresistors based on pure SnO_2 in the period from January 2015 to July 2020. In order to have a common background between all the considered responses, only test in dry air have been taken into account.

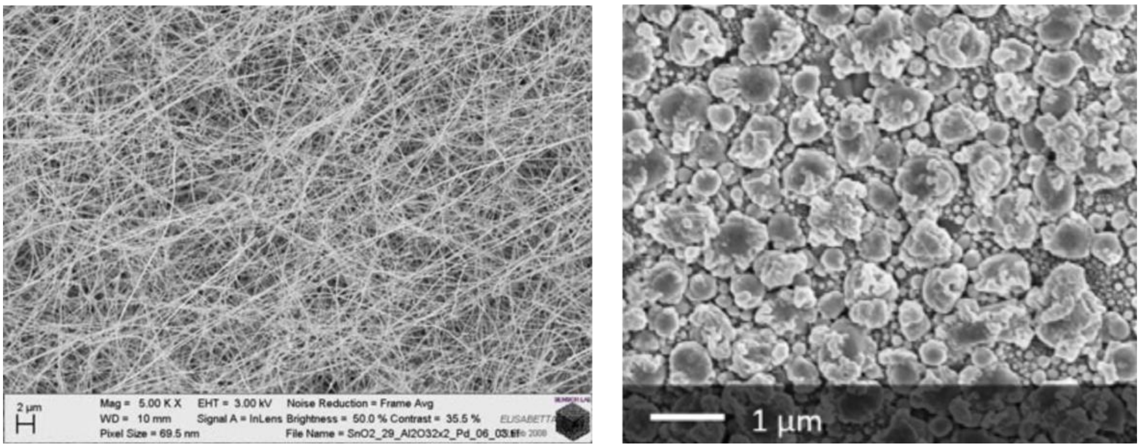
The morphology of the SnO_2 layer is described at two different levels: at the level of individual nanostructures and the level of their eventual hierarchical assembly.

Concerning the shape of individual crystallites composing the sensing layer, it has been categorized as follows:

- Nanorods: elongated nanostructures having a high aspect-ratio, with surfaces identified by well-defined crystalline planes;
- Nanoparticles: spherical nanostructures such as those used in thick films;
- Nanosheets: thin nanostructures extending in two dimensions.

3. Results

As an example of the shape of elementary nanostructures widely investigated in the literature, Figure 1 reports the SEM images for two SnO_2 layers composed by a disordered network of nanowires, Figure 1a, and by a disordered network of nanoparticles, Figure 1b, [1].



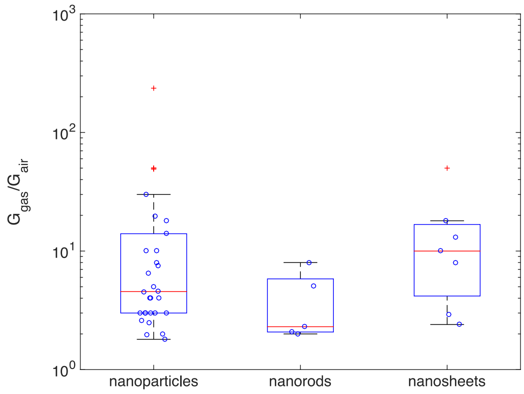
(**a**) (**b**)

Figure 1. Examples of two different morphologies investigated in the literature for SnO_2 based chemiresistors. (**a**) film composed by a disordered network of SnO_2 nanowires; (**b**) film composed by a disordered network of SnO_2 nanoparticles. Reprinted from [1].

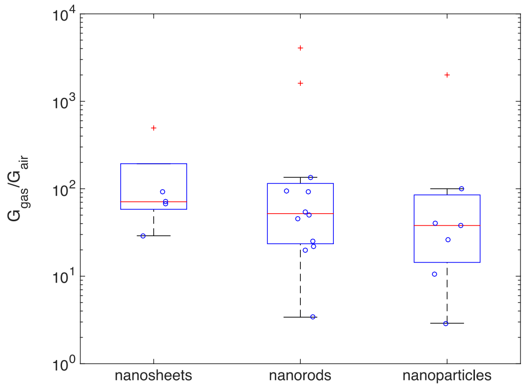
Boxplots resuming the responses to 10 ppm and to 300 ppm of ethanol reported in literature are shown in Figure 2a and 2b respectively, grouping the results by nanostructure morphologies, namely nanorods, nanoparticles and nanosheets.

The statistical parameters describing these distributions are reported in Table 1 and Table 2 for data shown in Figure 2a and 2b respectively.

Statistical parameters reported in these tables are: the number of samples considered in each category (morphology of elementary nanostructures), the number of outliers identified for each category, the values of the 1st, the 2nd and the 3rd quartiles (Q1, Q2 and Q3) of the response amplitude G_{gas}/G_{air}, the values of the upper and lower whiskers. The p-value of the median test comparing the median response of morphologies two by two are also reported in order to have a statistical check about the similarity/dissimilarity between median responses of the different morphologies.



(**a**)



(**b**)

Figure 2. Boxplots resuming the statistics of the response intensities of SnO_2 chemiresistors grouped by crystallite shape. (**a**) statistics recorded vs 10 ppm of ethanol; (**b**) statistics recorded vs 300 ppm of ethanol.

Table 1. Statistics of data shown in Figure 1a: responses to 10 ppm of ethanol.

	Nanoparticles	**Nanorods**	**Nanosheets**
Number of samples	30	5	7
Number of outliers	4	0	1
G_{gas}/G_{air}, Q1	3	2.075	4.175
G_{gas}/G_{air}, Q2 (median)	4.55	2.3	10
G_{gas}/G_{air}, Q3	14	5.825	16.75
G_{gas}/G_{air}, whisker low	1.8	2	2.4
G_{gas}/G_{air}, whisker up	30	8	18
p-value median test, nanorods	NaN	0.68	0.18
p-value median test, nanoparticles	0.68	NaN	0.08
p-value median test, nanosheets	0.18	0.08	NaN

Table 2. Statistics of data shown in Figure 1 (b): responses to 300 ppm of ethanol.

	Nanosheets	**Nanorods**	**Nanoparticles**
Number of samples	5	12	7
Number of outliers	1	2	1
G_{gas}/G_{air}, Q1	58.25	23.5	14.375
G_{gas}/G_{air}, Q2 (median)	71	52	38
G_{gas}/G_{air}, Q3	193	115	85
G_{gas}/G_{air}, whisker low	29	3.4	2.9
G_{gas}/G_{air}, whisker up	93	135	100
p-value median test, nanorods	NaN	0.5	0.08
p-value median test, nanoparticles	0.5	NaN	0.21
p-value median test, nanosheets	0.08	0.21	NaN

4. Discussion

The distributions of the response intensities shown in Figure 2 depend from the gas concentration. This is partially due to the fact that different authors often tested their sensors against different ethanol concentration so there is no a complete overlap between concentration used in different articles. In other words, the sensors whose response is shown in Figure 2a are not exactly the same sensors whose response is shown in Figure 2b. Nonetheless, despite these differences, a common feature is that no morphology is clearly more performing than other morphologies. Median tests reported in Tables 1 and 2 feature a p-value that is larger than 0.05 in all situations. This means that there is no clear evidence to reject the null hypothesis, i.e., there is no clear evidence to reject the hypothesis that the couple of morphologies under test are not distinguishable. The same is observed for other concentrations and also considering the eventual hierarchical organization of the individual nanostructures into assembleis such as hollow-spheres, fibers, hollow-fibers, etc. [4]. On the other hand, some materials emerge as outliers with respect to all morphologies. In Figure 2a, there are six outliers: four are the responses from layers composed by nanoparticles, namely [5–8], with response intensities of about 236, 50, 49, 50 to 10 ppm of ethanol and one composed by nanosheets [9] featuring a response $G_{gas}/G_{air} \approx 50$. As a reference, median responses to this ethanol concentration are around 4.55, 2.3 and 10 for nanoparticles, nanorods and nanosheets respectively. Concerning the concentration of 300 ppm, four outliers emerges: the nanoparticles synthesized by [10], two types of nanorods and the nanosheets developed by [11]. These materials feature responses of about 2000, 4070, 1609 and 495, compared with the median responses of 71, 52 and 38 for nanosheets, nanorods and nanoparticles respectively.

These results are reasonably due to the longer tradition of the synthesis of nanoparticles with respect those of nanowires and nanosheets. Such a longer experience may reasonably imply a more developed capability to effectively combine the many parameters underlying the sensing mechanism, which may counterbalance the advantages arising from the fine morphological tuning inherent in the more recent nanostructures.

Funding: his research was funded by Regione Lombardia and Fondazione Cariplo through the project EMPATIA@LECCO.

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

References

1. Ponzoni, A.; Comini, E.; Concina, I.; Ferroni, M.; Falasconi, M.; Gobbi, E.; Sberveglieri, V.; Sberveglieri, G. Nanostructured Metal Oxide Gas Sensors, a Survey of Applications Carried out at SENSOR Lab, Brescia (Italy) in the Security and Food Quality Fields. *Sensors* **2012**, 12, 17023–17045.
2. Lee, J.-H. Gas Sensors Using Hierarchical and Hollow Oxide Nanostructures: Overview. *Sens. Actuators B Chem.* **2009**, 140, 319–336.
3. Palma, S.I.C.J.; Traguedo, A.P.; Porteira, A.R.; Frias, M.J.; Gamboa, H.; Roque, A.C.A. Machine Learning for the Meta-Analyses of Microbial Pathogens' Volatile Signatures. *Sci Rep.* **2018**, 8, 3360.
4. Ponzoni, A. Morphological Effects in SnO_2 Chemiresistors for Ethanol Detection: A Review in Terms of Central Performances and Outliers. *Sensors* **2021**, 21, 29.
5. Lee, S.-H.; Galstyan, V.; Ponzoni, A.; Gonzalo-Juan, I.; Riedel, R.; Dourges, M.-A.; Nicolas, Y.; Toupance, T. Finely Tuned SnO_2 Nanoparticles for Efficient Detection of Reducing and Oxidizing Gases: The Influence of Alkali Metal Cation on Gas-Sensing Properties. *ACS Appl. Mater. Interfaces* **2018**, 10, 10173–10184.
6. Tricoli, A.; Pratsinis, S.E. Dispersed Nanoelectrode Devices. *Nat. Nanotechnol.* **2010**, 5, 54–60.
7. Li,H.;Chu,S.;Ma,Q.;Li,H.;Che,Q.;Wang,J.;Wang,G.;Yang,P.MultilevelEffectiveHeterojunctionsBasedonSnO2/ZnO 1D Fibrous Hierarchical Structure with Unique Interface Electronic Effects. *ACS Appl. Mater. Interfaces* **2019**, 11, 31551–31561.
8. Tofighi, G.; Degler, D.; Junker, B.; Müller, S.; Lichtenberg, H.; Wang, W.; Weimar, U.; Barsan, N.; Grunwaldt, J.-D. Microfluidically Synthesized Au, Pd and AuPd Nanoparticles Supported on SnO_2 for Gas Sensing Applications. *Sens. Actuators B Chem.* **2019**, 292, 48–56.
9. Zhou,Q.;Chen,W.;Li,J.;Tang,C.;Zhang,H.Nanosheet-AssembledFlower-likeSnO2HierarchicalStructureswithEnhanced Gas-Sensing Performance. *Mater. Lett.* **2015**, 161, 499–502.

10. NaderiNasrabadi, M.; Mortazavi, Y.; Khodadadi, A.A. Highly Sensitive and Selective Gd_2O_3-Doped SnO_2 Ethanol Sensors Synthesized by a High Temperature and Pressure Solvothermal Method in a Microreactor. *Sens. Actuators B Chem.* **2016**, 230, 130–139.
11. Firooz, A.A.; Mahjoub, A.R.; Khodadadi, A.A. Highly Sensitive CO and Ethanol Nanoflower-like SnO_2 Sensor among Various Morphologies Obtained by Using Single and Mixed Ionic Surfactant Templates. *Sens. Actuators B Chem.* **2009**, 141, 89–96.