Extended Abstract

Towards Low Temperature VOCs Chemoresistors: Graphene Oxide Versus Porphyrin-Based Materials [†]

Eleonora Pargoletti [1,2]**, Francesca Tessore** [1,2]**, Gabriele Di Carlo** [1,2]**, Gian Luca Chiarello** [1] **and Giuseppe Cappelletti** [1,2,]*****

[1] Dipartimento di Chimica, Università degli Studi di Milano, via Golgi 19, 20133, Milano, Italy; eleonora.pargoletti@unimi.it (E.P.); francesca.tessore@unimi.it (F.T.); gabriele.dicarlo@unimi.it (G.D.C.); gianluca.chiarello@unimi.it (G.L.C.)

[2] Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali (INSTM), Via Giusti 9, 50121, Florence, Italy

* Correspondence: giuseppe.cappelletti@unimi.it; Tel.: +39 0250314228

[†] Presented at the title, place, and date.

Abstract: The sensing of gas molecules is of fundamental importance for environmental monitoring, control of chemical processes, and non-invasive medical diagnostics based on human's breath analysis. Herein, the synthesis of hybrid materials (SnO_2/graphene oxide-GO and SnO_2/porphyrins composites) with ad hoc properties led to chemoresistors able to reduce the acetone sensing temperature guaranteeing acceptable LOD values. As such, boosted potentialities, especially in terms of tuned selectivity and low water interference, may be obtained.

Keywords: VOC chemoresistors; hybrid materials; low-T sensing

1. Introduction

Volatile Organic Compounds (VOCs) are a huge class of molecules emitted from a large variety of both biogenic and anthropogenic sources [1]. They are considered as a critical factor for air pollution, and they give rise to serious damages problems for both environment and human health [1,2] because of their easy diffusivity, volatility, and toxicity even at low concentrations [3]. Moreover, some VOCs, present in the human's breath can be considered as biomarkers of specific illness, as they are strictly correlated to several metabolic processes. Among them, acetone can be considered a biomarker for type I diabetes as its concentration in breath varies from 300 to 900 ppb in healthy people to more than 1800 ppb for diabetics [4].

For all these reasons, the monitoring of these compounds has become mandatory. A promising solution for the detection and quantification of VOCs consists in the implementation of chemoresistive gas sensors based on the electrical resistance variation of the sensing material in presence of target molecules. The key to face this challenge is the development of miniaturized chemical sensors capable of selective sensing of few ppb of VOCs giving stable and reproducible responses in the presence of high concentrations of interfering species, such as water vapor and other gases [5].

Notably, n-type semiconductor metal oxides (MOS such as SnO_2, WO_3, ZnO, and TiO_2) devices have been already used quite extensively for several applications. They are compact, low-cost, easy to produce and use, able to detect a wide variety of gaseous species [6,7]. Although these features make such kind of sensors a convenient alternative to the traditional and most sophisticated analytical techniques (*e.g.* mass spectrometry and gas chromatography), there are also some drawbacks. Specifically, they can only operate at high temperatures (200-400 °C), showing short lifetime and low selectivity, so that it is difficult to selectively analyze multiple species in complex matrices [3].

To overcome these problems, the coupling of metal oxides with other matrices (such as carbonaceous- or porphyrin-based materials) [8,9] seems to be the key factor to create nano-composites capable of sensing at low temperatures (< 100 °C) simultaneously achieving good selectivity and sensitivity (ppb level) towards a target compound.

Therefore, the present work is aimed at evaluating and comparing the sensing performances of SnO_2 coupled with different porphyrins and graphene oxide (GO) towards acetone molecules, at mild temperatures (150 °C and 75 °C) under UV light, in a fixed SnO_2/matrix weight ratio.

2. Materials and Methods

2.1. Hybrid Synthesis, Electrodes Preparation and Sensing Tests

SnO_2 nanoparticles was chosen to be grown onto graphene oxide (GO) material by following a very easy hydrothermal method, already reported in our previous works [6–8]. According to earlier studies, we adopted 32:1 salt precursor-to-GO weight ratio since it resulted as the optimal one in terms of sensing performances at low operating temperatures [3].

Three different Zn^{II} porphyrins were synthesized according to previous papers [10-12], namely ZnTPP, ZnTPP(F_{20}), and ZnTPP(F_{20}CN); their relative chemical structures together with the UV-Vis spectra in CH_2Cl_2 solution are reported in Figure 1. The UV-Vis pattern is the one typically observed for porphyrins metal complexes [13], with an intense ($\varepsilon \approx 10^5$ M^{-1} cm^{-1}) Soret or B band at 400-450 nm and two weaker ($\varepsilon \approx 10^3$ - 10^4 M^{-1} cm^{-1}) Q bands at 500-600 nm (see the inset in Figure 1).
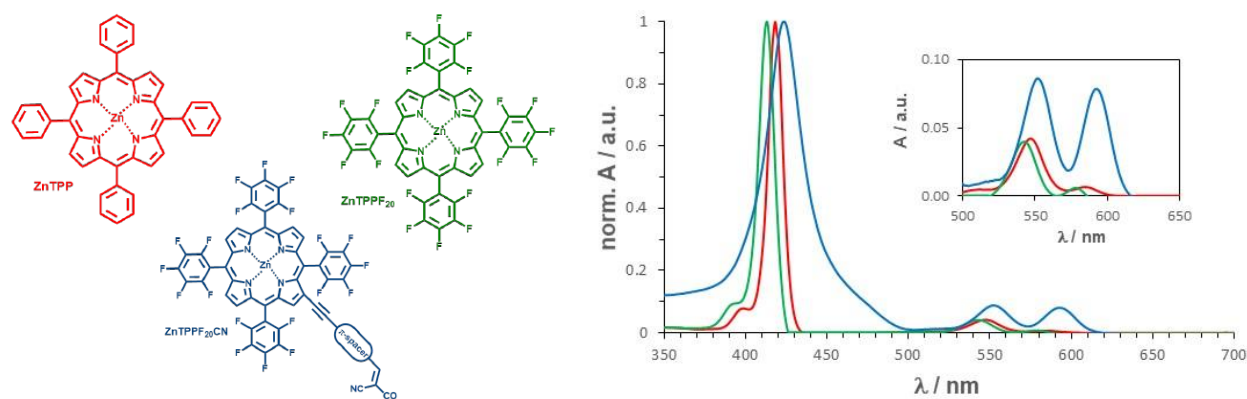

Figure 1. Investigated Zn^{II} porphyrins and their UV-Vis spectra.

Then, the SnO_2-porphyrin sensors have been obtained by depositing onto Pt-based interdigitated electrodes (IDEs) through a hot-spraying method [6-8] a first layer of porphyrin followed by a thin film of SnO_2. The mass ratio between SnO_2 and porphyrin is 32:1 as in the case of SnO_2/GO composite (verified by a microbalance). To this purpose, two dispersions have been prepared: a 0.6 mg mL^{-1} of the porphyrin and a 2.5 mg mL^{-1} of pristine SnO_2 both in EtOH.

Sensing measurements towards acetone at 150 °C and 75 °C under UV light (Jelosil HG500 lamp; effective irradiation power: 30 mW cm^{-2}) were performed adopting the chamber already described elsewhere [14]. The tests have been carried up to 150 °C since the porphyrin complexes degrade at higher temperatures [15]. The sensor response is reported as: $(R_{air}/R_{acetone}) - 1$, where R_{air} is the film resistance in air and $R_{acetone}$ is the film resistance at a given concentration of the acetone gas. We also computed the sensor response (t_{res}) and the recovery times (t_{rec}).

2.2. Powders and Porphyrins Characterizations 84

SnO$_2$ and SnO$_2$/GO samples were characterized by specific surface area measure- 85
ments (Micromeritics Tristar II 3020), X-Ray Powder Diffraction (XRPD, Philips PW 3710) 86
analyses and Diffuse Reflectance Spectroscopy (DRS, Shimadzu UV-2600) to evaluate 87
powders optical band gaps (E$_g$) by means of Kubelka-Munk equation [3,8]. 88

The goodness of the as-synthesized powders has been verified through ^{1}H- and ^{19}F- 89
NMR spectroscopy in CDCl$_3$. The NMR spectra are fully in agreement with the literature 90
[10-12]. 91

3. Results and Discussion 92

Hybrid sensing materials, such as SnO$_2$-porphyrins and SnO$_2$-graphene oxide com- 93
posites, arouse interest thanks to the possible complementary features between the two 94
components, showing a cooperative and synergistic behavior [6,9]. 95

Table 1. Surface area (*S*$_{BET}$), total pore volume (V$_{tot. pores}$), crystallite domain size by XRD analysis 96
(<d^{XRD}>) and optical band gap (E$_g$, by Kubelka-Munk extrapolation). 97

Sample	*S*$_{BET}$ (m^2 g^{-1})	V$_{tot. pores}$ (cm^3 g^{-1})	<d^{XRD}> (nm)	E$_g$ (eV)
GO	30	0.020	11	–
SnO$_2$	67	0.210	15	3.6
SnO$_2$/GO	55	0.133	8	3.4

98

In the case of SnO$_2$/GO hybrid, the formation of nano-heterojunctions with a three- 99
dimensional SnO$_2$ network has been verified by a combination of physical and chemical 100
characterizations. Specifically, Table 1 reports the specific surface area (*S*$_{BET}$) together with 101
total pores volume (*V*$_{tot. pores}$), the average domain size by x-ray diffraction analysis (<d^{XRPD}>) 102
and optical band gap (E$_g$) of pure SnO$_2$ and GO together with the composite (SnO$_2$/GO) 103
sample. Moreover, HRTEM, XPS, Raman and responsivity analyses (already reported in 104
our previous works [3,8]) corroborate that a nano-heterojunction occurs when tin oxide 105
particles are grown onto GO sheets, allowing an intimate contact between the semicon- 106
ductor and the graphene oxide matrix. This fact leads to a signal intensity of three times 107
higher with respect to that of the pure SnO$_2$ (Figure 2a) in the case of 20 ppm of acetone at 108
150 °C under UV light. Notably, the SnO$_2$/GO was able to reach a LOD of 100 ppb of ace- 109
tone thanks to the synergistic effect between n-type MOS and p-type GO [3,6]. Further- 110
more, the response (t$_{res}$ around 60 s) and recovery (t$_{rec}$ around 90 s) times seem to be com- 111
parable with those of pure SnO$_2$. 112

Then, the sensors obtained overlapping a SnO$_2$ and porphyrin layers were tested. 113
Specifically, to evaluate the effect of the porphyrin matrix on the sensing properties of 114
SnO$_2$, the responses of SnO$_2$/ZnTPP and SnO$_2$/ZnTPP(F$_{20}$) were compared to that of pris- 115
tine SnO$_2$ as shown in Figure 2a. The combination of SnO$_2$ with the ZnTPP porphyrin 116
matrix has undoubtedly a beneficial effect on the sensing performance, as reported in the 117
recent literature [9,15,16]. Li *et al.* observed that light has a beneficial influence in the gas 118
sensing by ZnO nanorods functionalized with porphyrins [16]. They asserted that light 119
activates a charge transfer from the porphyrin to the ZnO, simultaneously creating a de- 120
pletion of electrons which favors the charge transfer from the donor-absorbed species. 121

Moreover, the main interfering species in the gas sensing process is humidity, espe- 122
cially at low T: Chen *et al.* [17] observed that the moisture can adsorb on the semiconductor 123
oxide surface, interacting with the acetone molecules and leading to a dramatic change in 124
the final sensor behavior. Indeed, a fluorine modified porphyrin, named as 125
SnO$_2$/ZnTPP(F$_{20}$), was synthesized and tested since fluorine atoms may confer hydropho- 126
bic character leading to a possible reduction of the water interference. Unfortunately, no 127
positive results were obtained, the signal intensity is halved compared to that of the pure 128
SnO$_2$ powders, probably due to the strong electron density attractor capability of F-groups 129
[10-12]. Notably, the sensor response of SnO$_2$/ZnTPP(F$_{20}$CN) at 150 °C (Figure 2a) is the 130

most intense one among the tested hybrid materials, since this Zn^{II} porphyrin carries a cyano-acrylic moiety able to bind SnO_2 and to impart a proper directionality to charge-injection [11-12]. Moreover, the CN group acts as a buffer towards the strong electron acceptor behavior of F atoms, guaranteeing concomitantly the desired hydrophobicity to prevent the water interference. All the porphyrin-based sensors reached LOD values of 200 ppb at 150 °C, notwithstanding an increase of the response times of around 25-30% and the recovery times significantly longer (around 200 s).
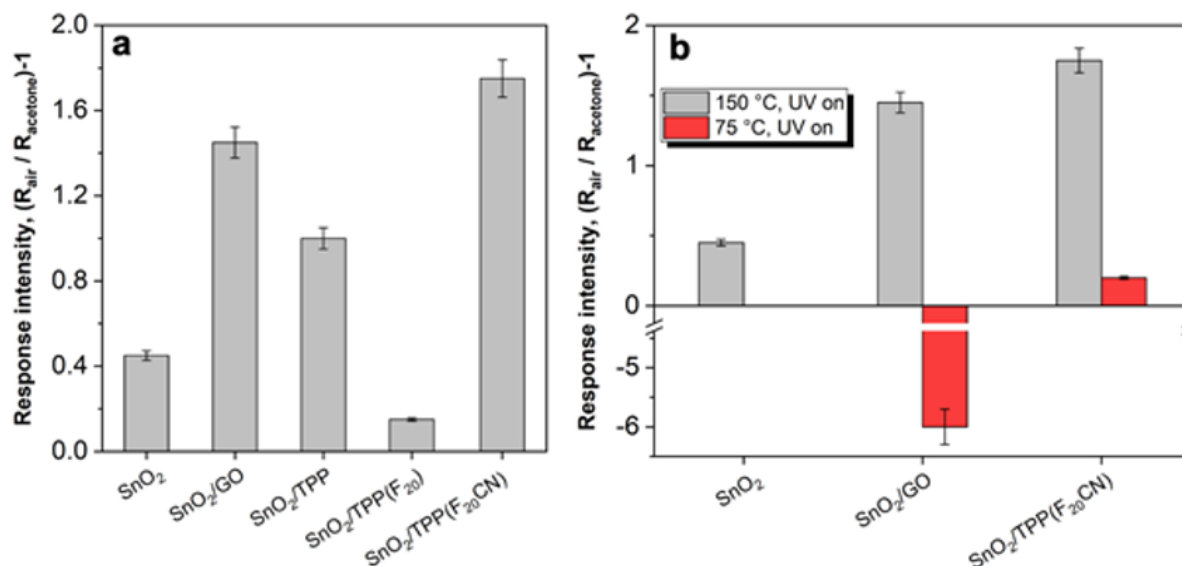

Figure 2. Sensors response intensities for both pure SnO_2 and hybrid materials towards 20 ppm of acetone under UV light at (a) 150 °C and (b) 75°C.

Finally, further tests were carried out at 75°C: while no acetone response (20 ppm) was appreciable in the case of pure SnO_2, a reversed behavior in conductance with SnO_2/GO sample occurred. This phenomenon is reported to be typical of metal oxide semiconductors operating at low temperatures due to a greater amount of adsorbed oxygen species and moisture [17]. Instead, under these conditions SnO_2/ZnTPP(F_{20}CN) produces a positive response, even if the LOD is 600 ppb, corroborating the synergistic effect of the fluorine species and the anchor group.

We believe that these findings can provide guidelines for the engineering of miniaturized chemoresistive sensors for low-temperature detection of acetone molecule. The excellent performances of the SnO_2-GO nano-heterojunctions and especially of SnO_2/ZnTPP(F_{20}CN) composite can pave the way for the development of tunable low-cost materials for fabrication of optoelectronic devices for various applications.

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