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Al-doped ZnO Gas Sensors Toward Safe and Effective Monitoring in Delicate Environments

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Summary:
In delicate environments, harmful gases may put both human health and sensitive materials at risk. Indeed, effective monitoring of hazardous compounds must be conducted without affecting the surroundings. In these circumstances, visible-light photoactivated metal-oxide semiconductor gas sensors are a suitable alternative to their thermo-activated counterparts. Al-doped ZnO emerges as a promising material for sustainable gas sensors in such applications.

Keywords: chemoresistive gas sensors, photo-activation, cultural heritage, aluminum metal doping, environmental monitoring

Introduction

Atmospheric pollutants have been demonstrated not only to compromise human health, but also to negatively affect the permanence and integrity of materials, especially in sensitive environments, such as museums [1]. In these settings, objects, staff, and visitors must be protected against the presence of hazardous gases. This highlights the necessity of new gas sensing technologies, which must be portable, user-friendly and non-invasive, hence able to discriminate analytes without compromising the site. Nowadays, sustainability is another crucial concern. In this context, it refers to both the synthesis of the sensing materials and how they operate, with the use of abundant and low-toxic elements, and employing sensors with low energy consumption. To this end, visible-light photoactivated metal-oxide semiconductor (SMOXs) gas sensors represent a viable alternative to their well-established thermally activated counterparts, which involve high temperatures (200-500°C). However, the performance of the latter tends to be inadequate for applications, due to low response values, slow kinetics, and non-reversibility of the signal, also caused by a lack of knowledge on the gas sensing mechanism in this regime [2]. Furthermore, as wide-bandgap semiconductors, most SMOX materials require UV light for photo-activation, which then is the most used source even if it features low efficiency, high energy consumption and may lead to the destruction of analytes. In this framework, ZnO is a widely studied material both in thermo- and photoactivation, typically functionalized with noble metals [2] in order to enhance and tune the material sensing properties. ZnO functionalization by innovative metal doping, such as aluminium, could enable the generation of inter-gap states [3], making this SMOX a good candidate for a visible-light activated sensor. Additionally, aluminum is an abundant and safe element, making it a sustainable choice for the development of efficient and environmentally friendly gas sensors.

Materials and methods

For this purpose, aluminum doped zinc oxide (Al:ZnO) was synthesized by a sol-gel approach. It was prepared with two different molar concentrations of Al (3% and 5%) and each of them was calcined at three different temperatures, namely 450, 500 (Fig.1), and 600 °C.

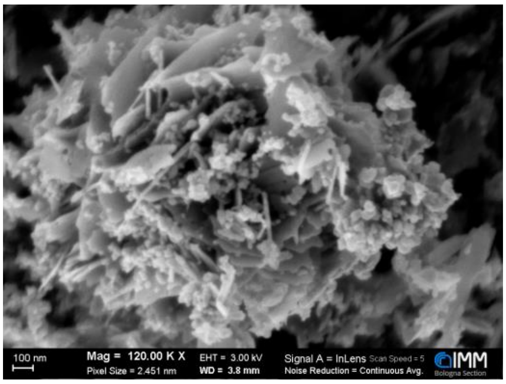

Fig. 1. Scanning Electron Microscopy (SEM) image of Al:ZnO, 5% of Al concentration, calcined at 500 °C.

Results and further perspectives

The sensors have been studied in dry air condition, and then were tested with NO_2 (0.5 ppm), toluene (10 ppm), benzene (0.5 ppm), NH_3 (10 ppm), acetaldehyde (0.5 ppm), and acetone (50 ppm), analytes of particular relevance in museums and archives. The tests were carried at three different operating temperatures, namely 200, 300, and 400 °C. The sensors exhibited a selectivity based on the operating temperature, as presented in Tab.1.

Tab. 1: Best sensor responses (R) obtained for each gas at 300, 400, and 600 °C. For each operating temperature, the best-performing sensor among the tested is reported.

Gas	*R* at 200°C	*R* at 300°C	*R* at 400°C
NO_2	5.5 Al5%600°C	0.6 Al5%500°C	2.3 Al3%600°C
Toluene	none	8.5 Al3%500°C	saturated
Benzene	0.1 Al3%600°C	1.2 Al5%500°C	3.7 Al5%500°C
NH_3	1.6 Al3%600°C	3.9 Al5%600°C	saturated
Acetald.	none	saturated	9 Al5%500°C
Acetone	12 Al5%600°C	saturated	saturated

In preliminary investigations, under blue-light activation (468 nm) at room temperature (RT) in dry air, the most promising sensor was Al:ZnO with 5% of aluminum, calcinated at 500°C. As shown in Fig. 2, the sensor exhibited fast response and recovery kinetics, with a response time of 2 min to 0.1 ppm of NO_2 and a recovery time, from the injection of 0.2 ppm of NO_2, of 9 min.

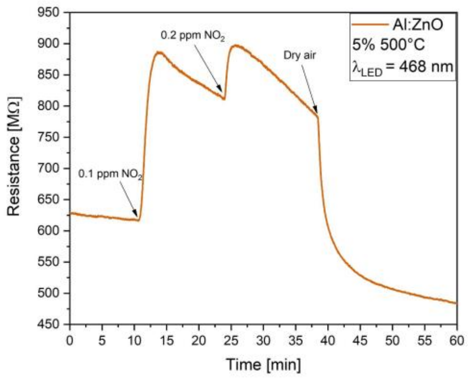

Fig. 2. Electrical resistance of Al:ZnO sensor (5% Al, calcinated at 500 °C) under blue-light activation (468 nm) at RT in dry air, exposed to 0.1 and 0.2 ppm of NO_2.

This study demonstrates the potential of combining material sustainability with technological advancements in gas sensors, paving the way for applications in delicate environments, such as cultural heritage sites. Further studies will be conducted on the performance and the gas sensing mechanism in thermo- and photo-activation regime, through the *Operando Diffuse Reflectance Infrared Fourier Transform* spectroscopy apparatus at disposal of the University of Ferrara.

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