

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

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## Summary:

In environmentally fragile settings, 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 thermoactivated counterparts. Al-doped ZnO emerges as a promising material for more 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 environmentally fragile sites, 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 space. 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, their performance tends to be inadequate, 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 photoactivation, making it the most used source despite its low efficiency, high energy consumption and potential 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 aluminum, 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 more 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.

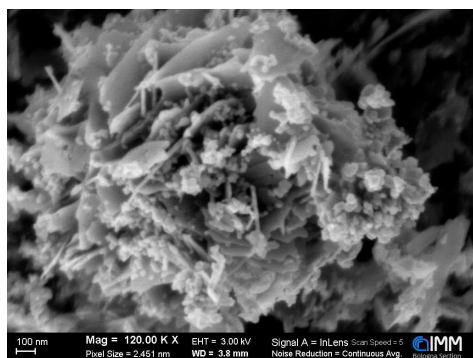


Fig. 1. Scanning Electron Microscopy (SEM) image of Al:ZnO, 5% of Al concentration, calcined at 500 °C.

### Results and further perspectives

The sensors have been studied in dry air condition, and then were tested with NO<sub>2</sub>, toluene, benzene, NH<sub>3</sub>, acetaldehyde, and acetone, analytes of particular relevance in museums and archives [1]. 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	<i>R</i> at 200°C	<i>R</i> at 300°C	<i>R</i> at 400°C
NO <sub>2</sub>	5.5 Al5%600°C	0.6 Al5%500°C	0.3 Al5%500°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 <sub>3</sub>	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<sub>2</sub> and a recovery time, from the injection of 0.2 ppm of NO<sub>2</sub>, of 9 min.

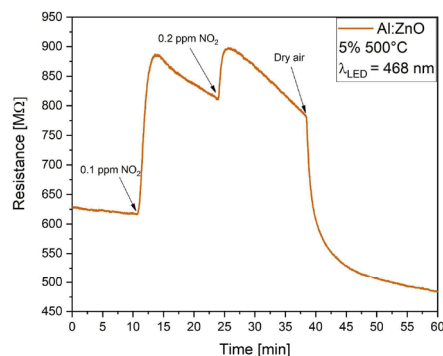


Fig. 2. Electrical resistance of Al:ZnO sensor (5% Al, calcinated at 500 °C) under blue-light activation (468 nm) at RT in dry air, exposed to 0.1 and 0.2 ppm of NO<sub>2</sub>.

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

### References

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### Acknowledgements

E. Tavaglione scholarship in Physics is funded by the D.M. n. 118/2023, supported by PNRR - funded by the UE - NextGenerationEU - Mission 4 “Education and Research” - Component 1 “Strengthening the offer of educational services: from nursery schools to university” - Investment 4.1 PNRR scholarships for Cultural Heritage.