

Tin Oxide Based Nanomaterials for Gas/VOC Sensing

A Thesis submitted by
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Summary and Future Outlook

The high operating temperature and humidity intolerance are metal oxide-based chemiresistive sensor bottlenecks. This thesis evaluated the influence of various methodologies on the sensing performance of SnO₂ nanomaterials, including nanocomposite with carbon nanomaterial, nanocomposite with metal, nano structuring with porosity control, and non-metal doping. After optimizing the different synthetic parameters, the development of low-temperature operable and humidity-tolerant gas/VOC sensors was successfully achieved. The thesis work is summarized in the upcoming section.

7.1 Summary

Chapter 1 gives an overview of the importance of metal oxide semiconductors for gas/VOCs sensing applications. A detailed literature survey of the synthesis and the application of SnO₂ nanomaterials for Nitrogen dioxide, Xylene and Ammonia sensing is also discussed.

In **Chapter 2**, the characterization techniques and the sensing device fabrication used in the thesis are detailed. A brief introduction to the electrochemical methods and techniques is also presented.

Chapter 3 focuses on the synthesis of SnO₂-rGO at optimized conditions by the solvothermal method. In SnO₂-rGO nanohybrid device identified through a combinatorial approach, optimum morphology and structure along with the intrinsic Sn-C bond exhibited a significant response of ~3 to a low concentration of 80 ppm NO₂ at room temperature operation and fluctuating humidity (20-50% RH) at much faster speeds ~5.6 s and recovered quickly in 14.1 s without heating. The SnO₂-rGO hybrid resulted in a highly selective, repetitive, and reproducible response with an RSD of ~0.9 % for NO₂ with a negligible response to interfering gases/VOCs at room temperature.

In **chapter 4**, synthesized Sn-SnO₂ as a sensing material with unique mesoporous nano-spherical morphology, providing a high specific surface area for gas/VOC adsorption. The sensor exhibits a repeatable response of 255% at 60 ppm xylene with unprecedented ultrafast response and recovery time of 1.5 s and 40 s, respectively. The Sn metal plays the catalytic role for enhanced selectivity, while nano spherical morphology enhances the sensor's sensitivity. This work opens new pathways for developing metal oxide-based sensing materials with humidity-tolerant characteristics.

In **chapter 5**, we developed freestanding SnO₂ nanosheets synthesized by a facile solvothermal method for ammonia detection at room temperature under extreme moisture content. The best sensing device demonstrated high sensitivity to ammonia (150% at 100 ppm) with fast response (8 s) and recovery (55 s) kinetics, as well as impressive selectivity against a variety of reducing and oxidizing agents at a temperature of 25 °C and relative humidity (RH) of 70%. A theoretical LOD of 64 ppt implies superior sensitivity to all previously reported SnO₂-based chemiresistive sensors. The improved sensing characteristics were attributed to the large specific surface area, defects, and porous structure of SnO₂ nanostructures. This study offers possibilities for highly sensitive, selective, and reliable rapid ammonia detection in environmental monitoring and medical diagnostics.

In **chapter 6**, the optimized substitutional fluorine doping in SnO₂ film results in high conductivity, hydrophobicity, transparency, reduction in oxygen defects, and excellent electrochemical stability. Consequently, the fabricated F-SnO₂ sensor showed a humidity-

resistant nature with the highest response of 52% towards triethylamine at a relatively low operating temperature.

7.2 Future Scope of the Work

Chemical sensing is the most important research sectors as the comfortable existence of the human generation is highly dependent on this field. Surface functionalization, nano structuring, nano compositing, and defect engineering as a step towards tailoring the properties of SnO₂ nanomaterials for enhanced properties in gases/VOCs sensing applications is successfully undertaken in this thesis. Consequently, the significant improvements observed in the performance of Nitrogen dioxide, Xylene, Ammonia, and Triethylamine sensing are indeed noteworthy.

The future prospects of the thesis works are as follows:

- The in-depth effect of device size and geometry on the sensing performance will be studied. So, these sensors can be deployed for real-time measurements of environmental gases/VOC after miniaturization and integration with the AIoT platform.
- An electronic nose can be developed by utilizing the developed sensing materials library for early disease diagnosis from the exhaled breath.
- The SnO₂-rGO and SnO₂-MWCNTs sensing material was further successfully explored for simultaneous detection of Cd²⁺, Pb²⁺ and Cu²⁺, Hg²⁺ respectively directly from intentionally spiked deionized water. The electrodes also demonstrate exceptional selectivity and sensitivity even under complex metal ion environment and thus was tested for heavy metal ion sensing directly in tap water (Verma, M. et al., 2023, Manuscript under preparation).
- The concept of direct chemical bonding in SnO₂-rGO nanocomposites can be extended to the formation of highly efficient nanocomposites for energy, sensing, and environmental applications.
- The concept of in-situ Sn doping of SnO₂ developed in the study can be extended to other metal oxide nanomaterials. Further, the control over Sn content for tuning sensing performance can also be explored.
- The synthesized SnO₂ nanosheets by pH optimization method can be further used in energy storage applications.
- The concept of fluorination can be explored for other metal oxides for development of better sensors.