



Mixed Oxides as VOCs Detectors in Biomedical Applications

Dinu Litra^(✉) , Cristian Lupan , Nicolae Magariu , Adrian Bîrnaz ,
and Oleg Lupan 

Center for Nanotechnology and Nanosensors, Department of Microelectronics and Biomedical Engineering Technical, University of Moldova, 168 Stefan cel Mare Av., MD-2004 Chisinau, Republic of Moldova

`dinu.litra@mib.utm.md`

Abstract. Mixed nanostructures based on zinc oxide (ZnO), copper oxide (CuO) and iron oxide (Fe₂O₃) were synthesized through thermal oxidation in air, and their gas sensing properties were investigated. The motivation for combining these oxides lies in their complementary semiconductor behaviour: ZnO and Fe₂O₃ are n-type materials, while CuO is a p-type material. Forming p–n junctions enhances charge transfer and increases surface reactivity, thereby improving sensitivity and selectivity. Structural characterization using scanning electron microscopy (SEM) revealed interconnected nanostructures with sponge-like morphologies. Gas sensing experiments were conducted using a Keithley 2400 source meter to evaluate the sensor response towards n-butanol, 2-propanol and acetone at concentration of 100 ppm within a temperature range of 22–275 °C. The highest response was observed for 2-propanol, followed by acetone and n-butanol, with optimal performance at 250–275 °C. Response and recovery times were found to be in the range of a few to tens of seconds, indicating good reversibility and repeatability. The sensing mechanism is governed by the interaction of adsorbed oxygen species (O_2^- , O^- , O^{2-}) with target gases, leading to electron release and changes in conductivity. The promising performance in detecting acetone highlights the biomedical potential of these mixed nanostructures, particularly for non-invasive breath analysis related to diabetes monitoring.

Keywords: ZnO · CuO · Fe₂O₃ · sensors · nanostructures

References

1. Hsu, C.L., Chen, K.C., Tsai, T.Y., Hsueh, T.J.: Fabrication of gas sensor based on p-type ZnO nanoparticles and n-type ZnO nanowires. *Sens. Actuators B Chem.* **182**, 190–196 (2013). <https://doi.org/10.1016/J.SNB.2013.03.002>
2. Xuan, J. et al.: Low-temperature operating ZnO-based NO₂ sensors: a review. *RSC Adv.* **10**, 39786–39807 (2020). <https://doi.org/10.1039/D0RA07328H>
3. Hansen, B.J., Kouklin, N., Lu, G., Lin, I.K., Chen, J., Zhang, X.: Transport, analyte detection, and Opto-electronic response of p-type CuO nanowires. *J. Phys. Chem. C.* **114**, 2440–2447 (2010). <https://doi.org/10.1021/JP908850J>
4. Bandgar, D.K., Navale, S.T., Khuspe, G.D., Pawar, S.A., Mulik, R.N., Patil, V.B.: Novel route for fabrication of nanostructured α -Fe₂O₃ gas sensor. *Mater. Sci. Semicond. Process.* **17**, 67–73 (2014). <https://doi.org/10.1016/J.MSSP.2013.08.016>
5. Tang, H., Matin, M.A., Wang, H., Al-Jassim, M., Turner, J., Yan, Y.: Synthesis and characterization of magnesium-alloyed hematite thin films. *J. Electron. Mater.* **41**, 3100–3106 (2012). <https://doi.org/10.1007/S11664-012-2205-4/METRICS>
6. Sharmin, M., Podder, J.: Band gap tuning, n-type to p-type transition and ferrimagnetic properties of Mg doped α -Fe₂O₃ nanostructured thin films. *J. Alloys Compd.* **818**, 152850 (2020). <https://doi.org/10.1016/J.JALLCOM.2019.152850>
7. Wang, Y., Kong, F., Zhu, B., Wang, S., Wu, S., Huang, W.: Synthesis and characterization of pd-doped α -Fe₂O₃ H₂S sensor with low power consumption. *Mater. Sci. Eng. B.* **140**, 98–102 (2007). <https://doi.org/10.1016/J.MSEB.2007.04.004>

8. Karuppasamy, K. et al.: Room-temperature response of MOF-derived pd@PdO core shell/ γ -Fe₂O₃ microcubes decorated graphitic carbon based ultrasensitive and highly selective H₂ gas sensor. *J. Colloid Interface Sci.* **652**, 692–704 (2023). <https://doi.org/10.1016/J.JCIS.2023.07.046>
9. Serrano, A. et al.: Improving the CO and CH₄ gas sensor response at room temperature of α -Fe₂O₃ (0001) epitaxial thin films grown on SrTiO₃ (111) incorporating au(111) islands. *Coatings*. **11**, 848 (2021). <https://doi.org/10.3390/COATINGS11070848>
10. Cuong, N.D. et al.: Facile synthesis of α -Fe₂O₃ nanoparticles for high-performance CO gas sensor. *Mater. Res. Bull.* **68**, 302–307 (2015). <https://doi.org/10.1016/J.MATERRESBULL.2015.03.069>
11. Hjiri, M., Aida, M.S., Neri, G.: NO₂ selective sensor based on α -Fe₂O₃ nanoparticles synthesized via hydrothermal technique. *Sensors*. **19**, 167 (2019). <https://doi.org/10.3390/S19010167>
12. Chakraborty, B. et al.: Ultra-selective hydrogen sensors based on CuO - ZnO hetero-structures grown by surface conversion. *J. Alloys Compd.* **1002**, 175385 (2024). <https://doi.org/10.1016/J.JALLCOM.2024.175385>
13. Zhang, B., Fu, W., Meng, X., Ruan, A., Su, P., Yang, H.: Synthesis of actinomorphic flower-like SnO₂ nanorods decorated with CuO nanoparticles and their improved isopropanol sensing properties. *Appl. Surf. Sci.* **456**, 586–593 (2018). <https://doi.org/10.1016/J.APSUSC.2018.06.150>
14. Litra, D., Chiriac, M., Ababii, N., Lupan, O.: Acetone sensors based on Al-coated and Ni-doped copper oxide nanocrystalline thin films. *Sensors*. **24**, 6550 (2024). <https://doi.org/10.3390/S24206550/S1>
15. Siebert, L. et al.: Facile fabrication of semiconducting oxide nanostructures by direct ink writing of readily available metal microparticles and their application as low power acetone gas sensors. *Nano Energy*. **70**, 104420 (2020). <https://doi.org/10.1016/J.NANOEN.2019.104420>
16. Lupan, O. et al.: Additive manufacturing as a means of gas sensor development for battery health monitoring. *Chem.* **9**, 252 (2021). <https://doi.org/10.3390/CHEMOSENSORS9090252/S1>
17. Lupan, O. et al.: Al₂O₃/ZnO heterostructure-based sensors for volatile organic compounds in safety applications. *ACS Appl. Mater. Interfaces*. **14**, 29331–29344 (2022). <https://doi.org/10.1021/ACSAMI.2C03704>
18. Kutukov, P. et al.: Influence of mono- and bimetallic PtOx, PdOx, PtPdOx clusters on CO sensing by SnO₂ based gas sensors. *Nano*. **8**, 917 (2018). <https://doi.org/10.3390/NANO8110917>
19. Lupan, O. et al.: Influence of CuO nanostructures morphology on hydrogen gas sensing performances. *Microelectron. Eng.* **164**, 63–70 (2016). <https://doi.org/10.1016/J.MEE.2016.07.008>
20. Hoppe, M. et al.: ZnAl₂O₄-functionalized zinc oxide microstructures for highly selective hydrogen gas sensing applications. *Phys. Status Solidi A*. **215**, 1700772 (2018). <https://doi.org/10.1002/PSSA.201700772>
21. Lupan, O., Postica, V., Gröttrup, J., Mishra, A.K., de Leeuw, N.H., Adelung, R.: Enhanced UV and ethanol vapour sensing of a single 3-D ZnO tetrapod alloyed with Fe₂O₃ nanoparticles. *Sens. Actuators B Chem.* **245**, 448–461 (2017). <https://doi.org/10.1016/J.SNB.2017.01.107>
22. Lupan, O. et al.: TiO₂/Cu₂O/CuO multi-nanolayers as sensors for H₂ and volatile organic compounds: an experimental and theoretical investigation. *ACS Appl. Mater. Interfaces*. **13**, 32363–32380 (2021). <https://doi.org/10.1021/ACSAMI.1C04379>
23. Mathew, M., Shinde, P.V., Samal, R., Rout, C.S.: A review on mechanisms and recent developments in p-n heterojunctions of 2D materials for gas sensing applications. *J. Mater. Sci.* **56**, 9575–9604 (2021). <https://doi.org/10.1007/S10853-021-05884-4>

24. Kamble, V.B., Umarji, A.M.: Gas sensing response analysis of p-type porous chromium oxide thin films. *J. Mater. Chem. C Mater.* **1**, 8167–8176 (2013). <https://doi.org/10.1039/C3TC31830C>
25. Lupan, O. et al.: Enhanced ethanol vapour sensing performances of copper oxide nanocrystals with mixed phases. *Sens. Actuat. B Chem.* **224**, 434–448 (2016). <https://doi.org/10.1016/J.SNB.2015.10.042>
26. Mishra, Y.K. et al.: Direct growth of freestanding ZnO tetrapod networks for multifunctional applications in photocatalysis, UV photodetection, and gas sensing. *ACS Appl. Mater. Interfaces.* **7**, 14303–14316 (2015). <https://doi.org/10.1021/ACSAMI.5B02816>
27. Luo, Y., Ly, A., Debliquy, M., Lahem, D., Zhang, C.: A novel low-concentration isopropanol gas sensor based on Fe-doped ZnO nanoneedles