

ONE-DIMENSIONAL METAL OXIDE NANOSTRUCTURES: H₂ GAS SENSORS

GWC Kumara¹ and RP Wijesundera²

Abstract

This article thoroughly analyses metal oxide nanostructures with one-dimensional properties and their utilisation in hydrogen (H₂) gas detection. In recent years, there has been an increasing interest in utilising the distinct characteristics of Metal Oxides (MOXs) Nanowires (NWs), Nanorods (NRs), and Nanotubes (NTs) to create advanced H₂ gas sensors with exceptional performance. The article examines the ways of synthesising these nanostructures, focusing on hydrothermal, solvothermal, and electrospinning processes due to their cost-effectiveness and ability to produce high yields. This article discusses the operation of hydrogen (H₂) gas sensors that utilize one-dimensional metal oxide frameworks that can perform effectively at both room temperature and low temperatures. Moreover, the research highlights the need to examine adjustable growth factors to enhance the efficiency of these nanostructures. Furthermore, this study comprehensively investigates the effects of decoration, functionalization, and doping techniques on boosting the chemical and physical characteristics of Metal Oxides (MOXs) that are useful in gas sensing functionality. The study proposes the necessity for future research to investigate the operational processes of metal oxide nanostructures, specifically in the setting of hybrid nanocomposites. Thorough investigations like this are essential for evaluating the effects of certain materials on the structure and form of the hybrid system. This review aims to offer substantial insights that will enhance the advancement of high-performance sensor devices tailored for the detection of hydrogen gas. Additionally, the review incorporates a perspective that illuminates the expected future research trends in the field.

Keywords: Gas Sensors, H₂ sensing, Metal Oxides (MOXs), One Dimensional Nanostructures

¹ Department of Physics and Electronics, University of Kelaniya, Kelaniya

Email: ckumara@kln.ac.lk

 <https://orcid.org/0000-0002-9507-4146>

² Professor, Department of Physics and Electronics, University of Kelaniya, Kelaniya

Email: palitha@kln.ac.lk

 <https://orcid.org/0000-0002-3223-5969>



Accepted the revised version: 25 November 2023

This work is licensed under CC BY-SA 4.0. To view a copy of this license, visit <http://creativecommons.org/licenses/by-sa/4.0/>

Introduction

According to the 2018 World Health Organization (WHO) report, air pollution is among the major environmental risks to living organisms (Kumar, 2020). So, it is crucial to continuously observe and measure the presence and levels of air pollutants precisely in order to prevent bodily ailments such as headaches, skin and eye irritation, coughing, and respiratory issues. Consequently, the need for high-performance solutions arises from the rising need for improved sensors that can detect environmental contaminants such as volatile/semi-volatile organic compounds (VOCs/SVOCs), hazardous gasses (NO_x , O_3 , H_2S , NH_3 , CH_4), particulates, and chemical compounds. To be considered valuable instruments for practical applications, these sensors must fulfill several essential criteria, including but not limited to high sensitivity, selectivity, stability, dependability, low power consumption, durability, cost-effectiveness, and user-friendliness.

Gas sensors are essential in various industrial, environmental, and medical applications as they immediately detect and monitor specific gases. Among the many materials investigated for gas sensing applications, low-dimensional nanostructured metal oxides (MOXs) have emerged as promising candidates due to their unique properties and enhanced performance. There are several types of gas sensors: optical, colourimetric, gas chromatography, acoustic, catalytic, capacitive, cantilever, and electrical, based on the gas sensing mechanism (Kumarage, 2023). Besides, traditional gas sensing materials often face sensitivity, selectivity, and response time limitations. In contrast, low-dimensional nanostructured MOXs, including nanowires, nanotubes, and nanosheets, exhibit remarkable electrical and surface properties that can be tailored for superior gas sensing performance.

The concept of utilising MOXs in gas-sensing applications originated in the early 1950s with the discovery of the alteration in the electrical conductivity of Ge when exposed to varying atmospheric conditions (Brattain, 1953). Typically, a gas sensor device (Fig. 1) is composed of three main components: (1) a system for delivering the gas, responsible for sampling, filtering, and preconditioning; (2) a system for detecting the analyte gas, comprising the sensing element that transforms the chemical interaction into an electrical signal (in this work). The third component is the computing system, which evaluates data and converts it into an interpretable format (Kumarage, 2023). This article primarily focuses on discussing the detection system, emphasising the sensing elements and active materials of the device.

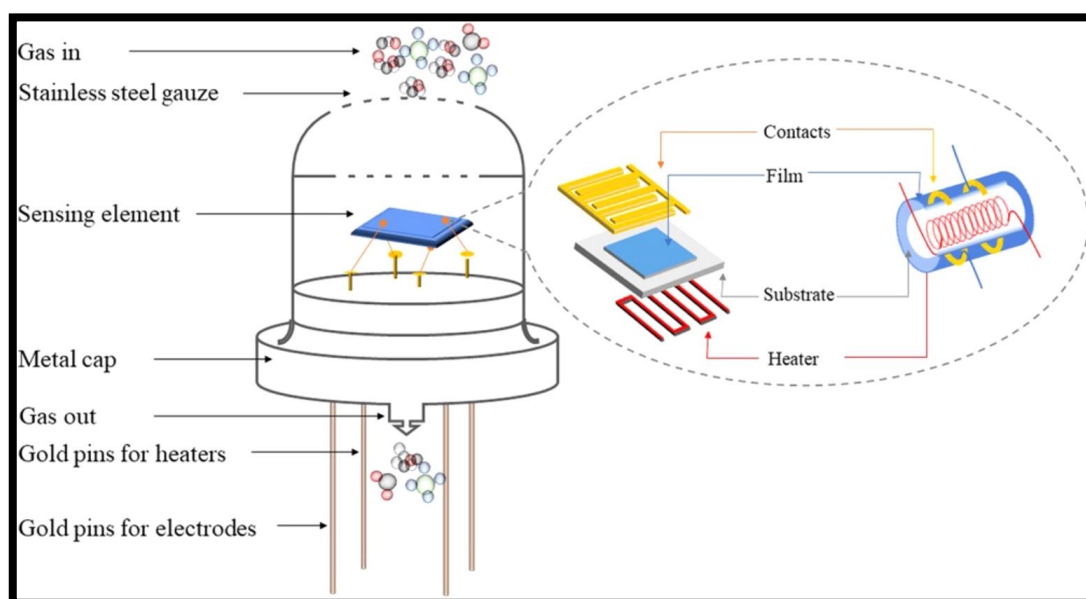


Figure 1: The general structure of the gas sensor. Reprint from [Kumarage, 2023].

MOXs semiconductors can be categorised into two distinct groups based on their predominant carriers. Specifically, in n-type MOXs: TiO_2 , Fe_3O_2 , ZnO , In_2O_3 , SnO_2 , and WO_3 , electrons constitute the majority carriers. On the other hand, p-type MOXs such as Co_3O_4 , Cu_2O , NiO , Mn_3O_4 , and Cr_2O_3 holes are the predominant carriers (Kumarage, 2021). Unlike the well-explored n-type MOX gas sensors, their p-type counterparts have received comparatively less attention, and the existing studies are still in an early stage of development (Fig. 2).

Hydrogen (H_2) is widely recognised as one of the most environmentally friendly and renewable energy sources. Nevertheless, the utilisation of H_2 faces challenges stemming from its inherently hazardous flammability and explosive properties under mild conditions in the case of leakage (Shi, 2021). Moreover, sensing H_2 through human sensory organs is complicated due to its colourless and odourless nature. Conventional detection methods are often intricate and involve expensive testing instruments. Therefore, the imperative lies in developing sensors for H_2 detection that offer ease of operation, cost-effectiveness, and outstanding performance in terms of sensitivity, selectivity, and stability. Addressing these challenges and enabling the practical detection of H_2 gas, MOXs nanomaterials have assumed heightened significance in gas sensor applications. This is attributed to their uncomplicated preparation methods, substantial surface area, heightened sensitivity, and cost-effectiveness.

This review discusses the basic concepts of gas sensing, focusing on the conductometric technique. This approach is based on the alteration in the electrical conductivity of the sensing material when it encounters various gases. The subsequent attention is directed towards the techniques used to produce metal oxides with low-dimensional nanostructures, investigating how these procedures affect the sensor's ultimate characteristics. In addition, this article discusses how different compositions and structures of metal oxides affect the performance of sensors. It provides a detailed summary of the latest advancements in H_2 sensing.

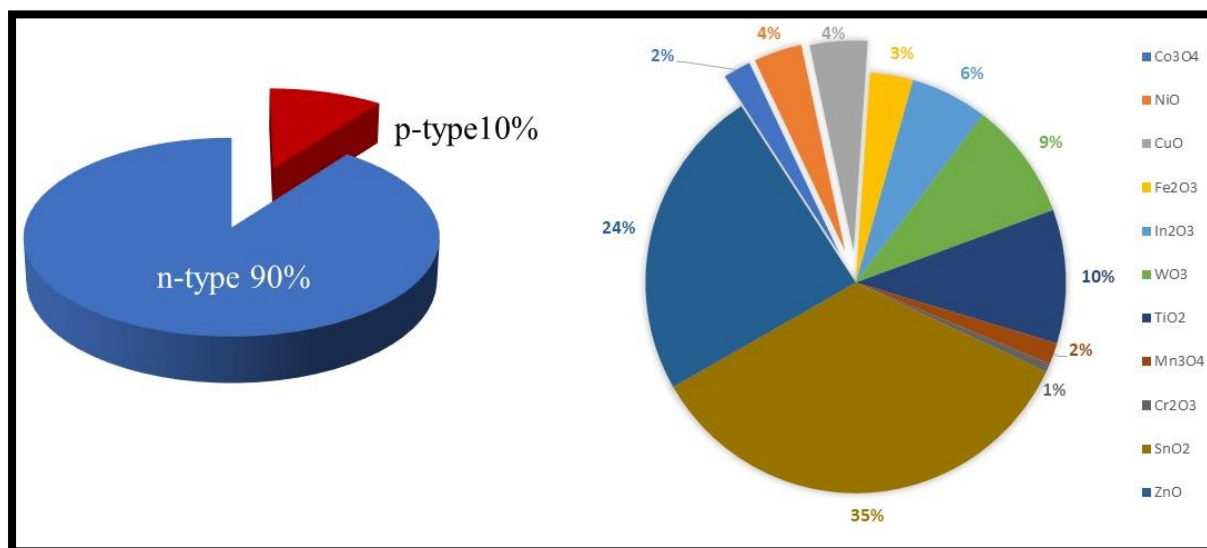


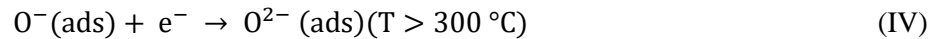
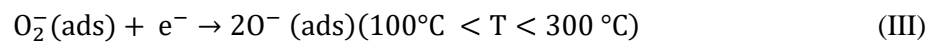
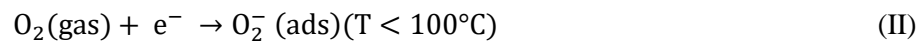
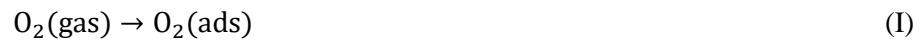
Figure 2: Employment of metal oxide in the conductometry gas sensing. Source: Web of Science.

Gas sensing mechanism and key functionality

A chemical sensor performs two primary functions: a receptor function and a transducer function. In the receptor role, the analyte compound engages with the surface of MOXs. Simultaneously, the transducer mechanism transforms a chemical signal into an electrical one in conductometric sensors. The gas-sensing mechanism of MOXs sensors relies on the ionosorption mechanism, which is based on

the modulation of the adsorption and desorption of oxygen species (O_2^- , O^- and O^{2-}) on the MOX surface. When MOXs are exposed to atmospheric air, oxygen molecules adhere to the MOX surface through two methods: physisorption and chemisorption. Physisorption, driven by van der Waals forces, involves no charge transfer between MOXs and oxygen. In chemisorption, oxygen molecules form tight bonds with MOXs due to charge transfer between them, making chemisorption a crucial step in the gas-sensing mechanism.

In this process, oxygen molecules interact with the conduction-band electrons of MOXs, generating oxygen species on the MOX surface. The type of oxygen species formed depends on the operating temperature of the sensors. For instance, O^- is formed at temperatures between 150 and 300 °C, while O^{2-} is formed at temperatures higher than 400 °C (Equation I-IV). When conduction-band electrons are captured by oxygen molecules, a depleted electron region forms on the MOX surface, causing an upward bend of the energy band in n-type MOXs (Fig. 3 a,b), resulting in reduced conductance. The presence of reducing gases (e.g., H_2 , CO , and CH_4) interacts with oxygen species, adding electrons to the conduction band and decreasing the depletion-layer width, causing a downward bend of the energy band and increasing conductance (Fig. 3 (c) and Equation V) (Shi, 2021). Conversely, conductance decreases in the presence of oxidizing gases (e.g., NH_3 and CO_2). However, the working principle is not as straightforward for complex molecules (C_2H_5OH and C_3H_6O).



The key parameters significant to the discussion on gas sensors encompass response, selectivity, response time, recovery time, stability, gas detection limit, and operating temperature. A brief comprehension of each parameter proves beneficial as a preliminary step before delving into an in-depth discussion on gas sensors.

Response, denoting the fraction of resistance on the sensing material when exposed to the analyte gas (R_g) compared to that in the air (R_a), is contingent upon factors such as crystallite size, porosity, operating temperature, and film thickness. Selectivity, governing the sensor's capacity to discern the target gas within a mixture, can be finely tuned by adjusting the operating temperature. However, it is noteworthy that MOX gas sensors may exhibit analogous responses to distinct gas molecules, thereby underscoring the critical role of selectivity in characterising sensing performance.

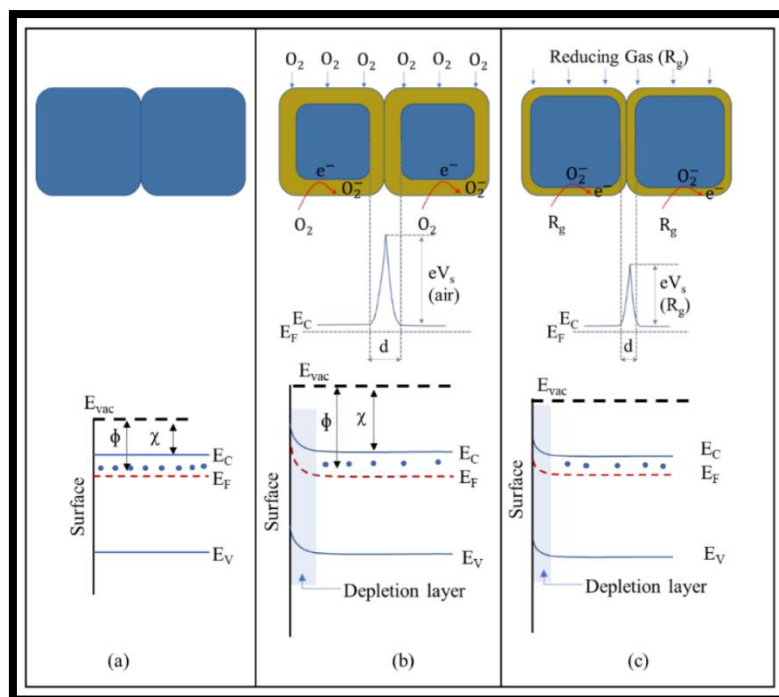


Figure 3: Energy-band diagram of a typical n-type MOX semiconductor: (a) flat band, (b) when an electron-depletion layer is formed due to chemisorption of oxygen molecules, and (c) when a reducing gas interacts with oxygen species. Reprinted from (Kumarage, 2023).

Stability pertains to the active material's ability to maintain its properties, such as electrical resistance in the context of conductometric sensors, consistently over time. Response time indicates the sensor's dynamic behavior in achieving a stable value for the monitored parameter, exemplified by the time required to reach 90% of the final resistance when exposed to the gas. The variation in electrical resistance of conductometric gas sensors during interaction with analyte molecules is typically illustrated in a dynamic response curve, showcasing the resistance/conductance alterations over time.

Recovery time, delineated as the interval necessary to return to 90% of the resistance value in the air after gas introduction, corresponds to the restoration of airflow. These parameters are ascertainable from the dynamic response plot. The detection limit denotes the minimum concentration of analyte gas detectable by the sensor. Finally, the working temperature designates the operational temperature of the sensor.

Growth Techniques of One-Dimensional Nanostructures

Two distinct methodologies, bottom-up and top-down, are employed to grow one-dimensional nanostructures. The top-down approach, encompassing the utilisation of conventional microfabrication equipment, involves the deposition and etching of planar structures to diminish their lateral dimensions to the nanoscale (Mijatovic, 2005). Various techniques, such as electron beams, focused ion beams, and X-ray lithography, have been applied in this context. Despite the notable advantages, such as leveraging well-established technology from the semiconductor industry and the convenience of direct preparation on planar substrates for subsequent electrical integration with the macro world, top-down approaches encounter challenges such as prolonged preparation times and significantly heightened costs.

The bottom-up synthesis process entails either the assembly of molecular building blocks or the direct chemical synthesis of nanoscale morphologies. The advantages of this method include high purity,

well-defined crystalline structure, and the ability to easily reach lower dimensions in the resulting materials. Moreover, it provides a cost-effective solution for experimental setups and allows for easy control of intentional doping and the development of devices using junctions (Kumarage, 2021; Kaur, 2018). However, there is a significant hindrance when integrating these materials onto flat surfaces to fully use their advantageous properties. Moreover, the organisation and positioning of nanostructures may provide difficulties (Krishna, 2022). Researchers have successfully utilised various methods, including the hydrothermal technique (Kumarage, 2023; Catto, 2023), sol-gel chemistry (Sztaberek, 2019; Xu, 2023), electrospinning (Fioravanti, 2022; Chen, 2022) and Vapor phase deposition (chemical, physical) (Galstyan, 2022), to grow MOXs nanowires for gas-sensing applications. These methods are preferred due to their simplicity, cost-effectiveness, and ability to produce consistent results. Each growth approach will be briefly described.

Hydrothermal and Solvothermal

The hydrothermal and solvothermal technique, renowned for its ability to synthesise, high yield, single crystals, low energy consumption, lower pollution, and easy control together with simple manipulation, relies on the notion of material solubility in a solution at high pressure (Yang, 2021). In general, both methods are similar. Solvothermal occurs in a nonaqueous solution (such as ethanol and ethylene glycol) at relatively high temperatures. The hydrothermal process is carried out in aqueous medium above the boiling point. During this procedure, a combination of precursors and solvent is placed in an autoclave for a prolonged period, creating crystal nuclei by applying heat and subsequent cooling (Kumarage, 2021). In the solution, metal ions create complexes with hydroxyl species, and as they lose water, solid metal oxide crystals are produced. Usually, the presence of a seed crystal is essential for the formation of one-dimensional nanostructures (Kumarage, 2023).

Sol-gel

The sol-gel procedure, first documented by Geffcken and Berger in 1939, has become an extensively utilised technique for fabricating diverse MOXs nanostructures (Liang, 2018). The sol-gel method consists of three main stages: the creation of a precursor solution, the development of a gel, and the ageing process (Kumarage, 2023). The procedure begins by subjecting a solution containing the precursor to hydrolysis, resulting in the formation of colloidal particles that are suspended in the solution. Subsequently, the condensation process occurs, resulting in the creation of a gel. The following phases encompass the processes of cleansing, dehydrating, and eventually subjecting to calcination in order to get a solid substance.

Electrospinning

Electrospinning is a widely employed method for synthesising nanoscale materials with a linear structure, specifically nanofibers. The electrospinning technique generates nanofibers or nanofibrous architectures within the size range of a few nanometers to a few micrometres. The variation depends on the composition of precursor solutions, electrospinning parameters, and environmental factors (Yang, 2021). During the electrospinning process, a solution, including polymers, is expelled from a minuscule aperture in a needle, driven by a powerful electric field generated by high voltage. The solution that has been evacuated undergoes either solidification or coalescence, forming a filamentous structure. The polymer-based precursor solution in the syringe becomes charged through the conductive metal needle connected to a high-voltage power source. As the precursor solution is gradually released from the needle, the intense electric field generated by the high voltage between the needle and the collector generates an electrostatic force that opposes the surface tension of the droplet at the needle opening. The force propels the charged precursor solution towards the electrically

grounded collector. Upon reaching the collector, the ejected solution undergoes solidification by solvent evaporation, creating solid nanofibers on the collector, as seen in Fig. 4.

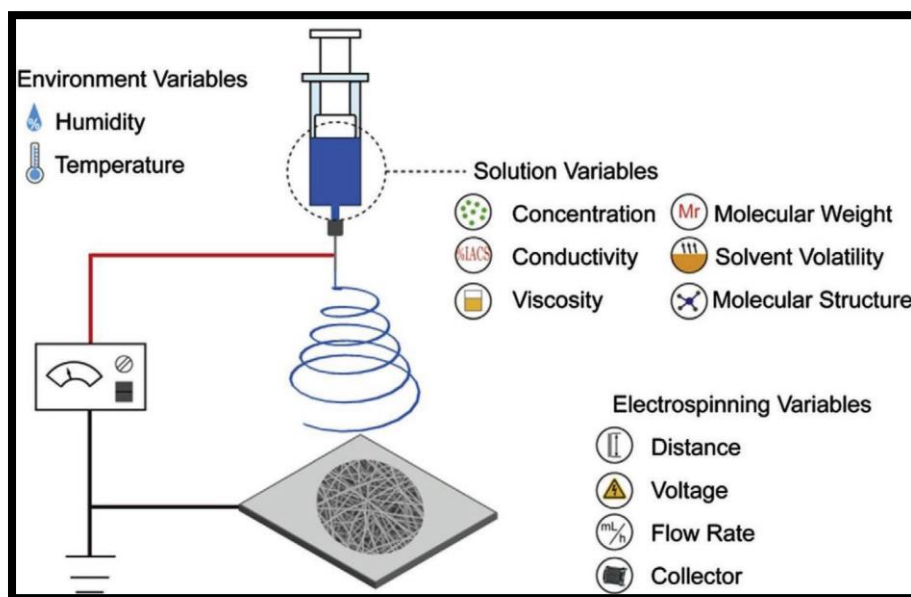


Figure 4: Schematic diagram of the electrospinning process. Reprinted from (Yang, 2021).

Vapor-phase Deposition

The vapour-phase approach includes many techniques that facilitate the production and growth of p-type MOX films. This method allows for precise control over the alteration of the crystal structure and thickness of the film. This method entails vaporising a substance source and its consequent deposition onto a substrate. The phenomenon of nucleation and subsequent growth occurs contingent upon the specific attributes of the reaction.

Physical vapour deposition (PVD) is a technique in which a material is evaporated and then condensed onto a substrate. Despite its high cost, PVD enables precise control over the thickness of thin films and the crystal structure and microstructure. Thermal evaporation, Magnetron sputtering, and molecular-beam epitaxy (MBE) are extensively researched methods of physical vapour deposition (PVD) (Moumen, 2022). Chemical vapour deposition (CVD) is a widely used technique for producing nanomaterials, including many forms of one-dimensional nanostructures. In the chemical vapour deposition (CVD) process, volatile precursors are carried to the reaction chamber in a controlled environment using a carrier gas. Upon entering, these initial substances experience breakdown on a heated surface, forming diverse nanomaterials. Chemical vapour deposition (CVD) is a commonly employed technique for fabricating nanowire or nanofiber structures and thin films (Anusiya, 2022). CVD may be categorised into several kinds, including plasma-enhanced chemical vapour deposition (PECVD) and low-pressure chemical vapour deposition (LPCVD).

H₂ Gas sensing properties

In recent advancements, various one-dimensional nanostructures, including nanowires (NWs) (Kumarage, 2023; Sisman, 2023; Kaur, 2023; Punginsang, 2022), nanorods (NRs) (Yusof, 2023; Patil, 2023; Sun, 2023), nanotubes (NTs) (Zakharova, 2018; Tasyurek, 2023; Wang, 2023), and nanobelts (NBs) (Kumarage, 2023; Chen, 2024; Tan, 2023), have been thoroughly investigated for numerous gas

sensing applications. However, this mini-review is limited to discussing the recent (within the last two years) gas-sensing applications of one-dimensional metal oxide on H₂ sensing.

Hydrogen, possessing flammability and explosiveness, becomes hazardous when its concentration surpasses 4%, as indicated by a high deflagration index (Moumen, 2022; Crowl, 2007). Therefore, it is crucial to detect H₂ to ensure its safe use, especially in energy-focused applications such as fuel-cell technology. Kumarage et al. have recently published a paper on the hydrogen sensing capability of Co₃O₄ NWs that were produced using thermal oxidation (Fig. 5). These nanowires have a diameter of 50 nm and a length ranging from 1 to 5 μm. At a temperature of 450 °C, the sensor has responded 232% to a concentration of 100 parts per million of H₂. In addition, the sensor has exhibited an atypical n-type sensing behavior due to the involvement of lattice oxygen in the gas-sensing process, which was triggered by the higher working temperature. Surprisingly, the sensors have retained a consistent level of electrical conductivity even when exposed to high levels of relative humidity (90%) for 25 days. The stability of the system has been ascribed to the catalytic prowess of Co₃O₄ and the elevated operational temperature (Kumarage, 2023). In the meantime, Lu and colleagues have documented a porous network comprising SnO₂ nanowires with an ultrasmall diameter of approximately 2 nm, designed for H₂ sensing. These SnO₂ nanowires were synthesised through a solvothermal process followed by annealing at 350 °C. The sensor exhibited a notable response of 13 to 40 ppm H₂ when operated at 250 °C, accompanied by a response time of 15 s and a recovery time of 31 s (Lu, 2021). Concurrently, Kumar et al. have presented findings on the potential for detecting H₂ at room temperature (RT) utilising Pd NWs. In this investigation, polycrystalline Pd NWs have displayed a response of 4.3% to 1 vol % H₂, with response and recovery times of 4.9 and 10.6 seconds, respectively.

On the other hand, quasi-single-crystalline Pd NWs demonstrated a response of 8% to 1 vol % H₂, with response and recovery times of 9.3 and 13.0 seconds, respectively. The polycrystalline Pd NWs have exhibited exceptional selectivity, stability, and sensitivity, achieving a limit of detection of 10 ppm H₂ in air. The rapid response of ultrathin polycrystalline Pd NW paper-based sensors can be attributed to the synergistic effects of their ultrasmall diameter, high-index surface facets, strain-coupled grain boundaries, and the porous paper substrate (Kumar, 2023).

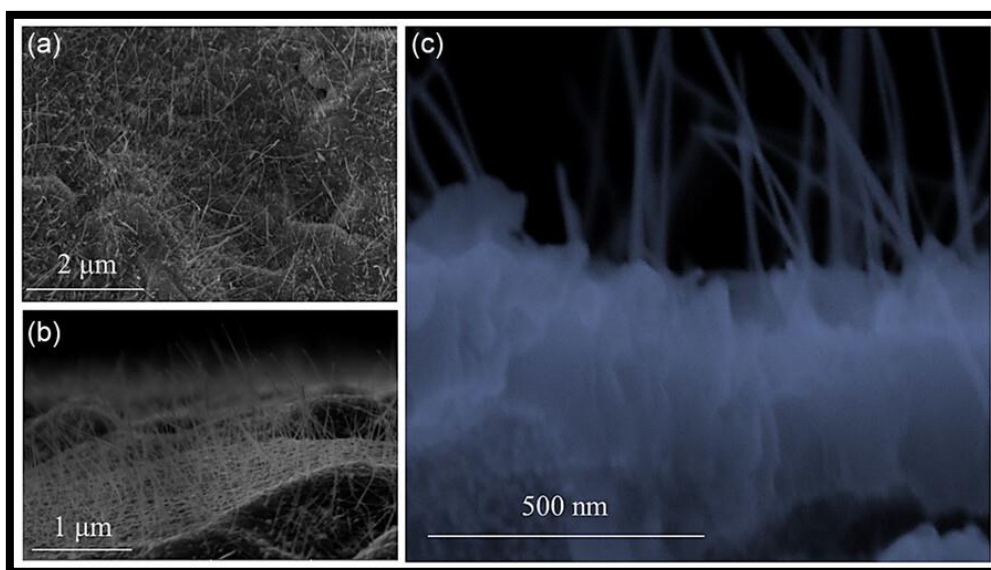


Figure 5: FESEM images of Co₃O₄ nanowires: a) 100 nm b) 50 nm, c) cross-sectional view of Co₃O₄ nanowires with initial Co thickness of 200 nm. Reprinted from (Kumarage, 2023).

The loading, decoration, and functionalisation of metal oxide gas sensors are fundamental strategies to augment their performance and sensitivity in gas detection applications. These techniques involve introducing or modifying nanomaterials on the surface of metal oxide sensors, aiming to optimise their gas-sensing characteristics, response kinetics, and selectivity. Integrating various catalysts, nanoparticles, or functional materials enhances the sensors' ability to detect specific gases at lower concentrations, operate at reduced temperatures, and exhibit improved stability.

For instance, the incorporation of palladium into SnO₂ nanowires has resulted in a noteworthy reduction in the operating temperature by 100 °C, concomitantly accelerating response and recovery times to 6 s and 3 s, respectively, due to the catalytic activity of Pd (Lu, 2021). In another study, Sennik et al. synthesised TiO₂ NRs of 100 nm diameter and 5 µm length, incorporating Pd for hydrogen detection at an operating temperature of 200 °C. These sensors demonstrated a remarkable 35-fold improvement in response compared to pristine TiO₂ NRs when detecting 1000 ppm H₂ (Sennik, 2016).

Similarly, an alternative investigation revealed a 2.79-fold enhancement in response by loading 10% In₂O₃ nanoparticles onto CeO₂ nanorods compared to pristine CeO₂ NRs when detecting 1000 ppm H₂ (Lv, 2023). Additionally, Chen et al. reported that loading 1.5% Pd onto In₂O₃ nanofibers (NFs) resulted in a response of 293.6 to 10,000 ppm H₂ at room temperature, accompanied by a response time of 12 s and a recovery time of 23 s. These exceptional gas sensing performances were ascribed to the catalytic property and chemical sensitisation of Pd and the high specific surface area arising from the porous structure (Chen, 2022).

In pursuit of enhancing the performance and tailoring the properties of metal oxide gas sensors for specific applications, researchers have adopted innovative strategies, notably doping and compositing. Doping entails introducing foreign elements into the metal oxide matrix, while compositing involves the amalgamation of metal oxides with other materials. These approaches are designed to optimise the sensor's selectivity, sensitivity, and response kinetics by capitalising on the distinctive electronic, catalytic, and structural characteristics of the introduced components. For instance, graphitic carbon nitride (g-C₃N₄)-doped zinc oxide NRs exhibit an excellent sensitivity (~53%) under H₂ gas exposure at RT, better than that of bare ZnO NRs (12%) (Fig.6). The results revealed that the fine incorporation of g-C₃N₄ into ZnO NRs on the planar silicon surface improves the H₂ gas sensing properties when compared to that of the planar silicon (PI-Si) surface. The doping of g-C₃N₄ into ZnO NRs increases the electrical conductivity through its graphene-like edges. In addition, the presence of defects in g-C₃N₄ induces the gas adsorption properties of ZnO through its active sites (Huang, 2022).

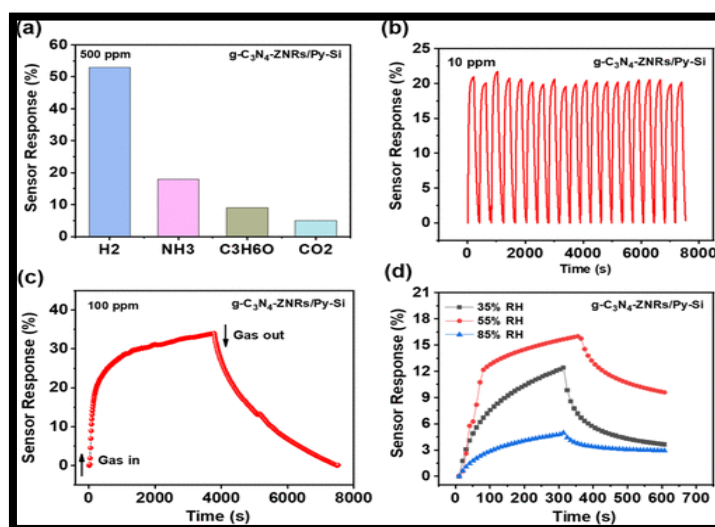


Figure 6: (a) Selectivity for different gases (at 500 ppm), (b) 20 repeated cycles, (c) stability in a 60 min on-off state, and (d) relative humidity (RH) of g-C₃N₄-ZNRs on pyramidal silicon (Py-Si). Reprinted from (Huang, 2022).

In a study by Lupam et al., ZnO nanowires were doped with Eu (10 μM), resulting in a remarkable 130-fold enhancement (7890) in the response when detecting 100 ppm H₂ (Lupam, 2022). In a separate investigation, Orhan and colleagues demonstrated the inversion of the p-type conductance of CuO nanowires through the deposition of a ZnO shell (10-20 nm) during H₂ detection at 400 °C (Sisman, 2023) (Fig 7). The inversion of the sensor signal and the lower response was discussed by a fully depleted shell layer and electrical field smearing effect (Fig.8). Table 1 summarises some recent advancement in H₂ sensing.

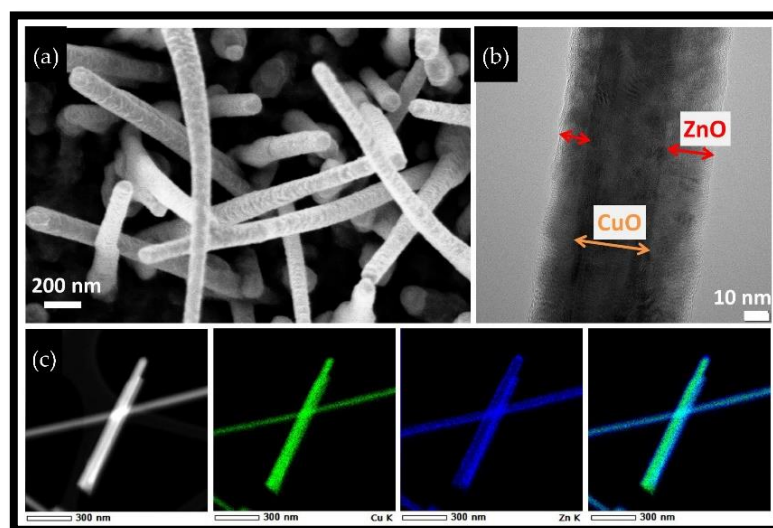


Figure 7: (a) FE-SEM, (b) HRTEM images of CuO–ZnO core–shell NWs and (c) overlay images by EDX measurement: copper in green and zinc in blue colours. Reprint from (Sisman, 2023).

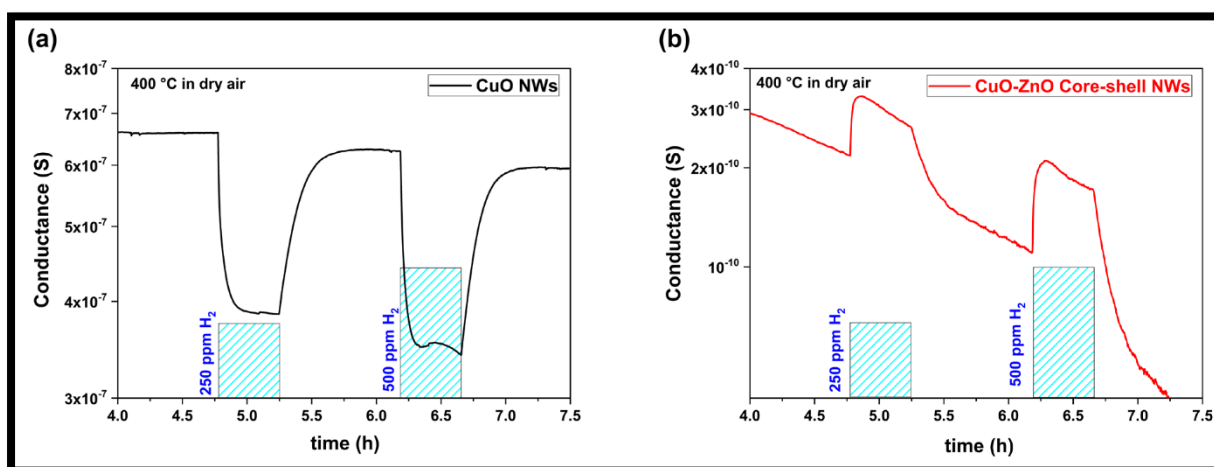


Figure 8: Isothermal dynamic response comparisons (a) CuO and (b) CuO-ZnO core–shell nanowires at 400 °C in dry airflow. Reprinted from (Sisman, 2023).

Table 1. Recent advancement in H₂ sensing.

Material	Struc.	Temp. (°C)	Conc. (ppm)	Res.	Tres/ Trec (s)	Repeatability/ stability	Ref.
Pd-coated SnO ₂	NRs	80	500	39.3	23 / 167	10 cycles / 70 days	(Jeong, 2023)
In ₂ O ₃ decorated CeO ₂	NRs	100	1000	14.8	N/A	N/A / 14 days	(Lv, 2023)
Zr-ZnO	NRs	RT	500	28%	N/A	3cycles / 18 days	(Shrisha, 2023)
g-C ₃ N ₄ -doped ZnO	NRs	RT	500	52.7 %	19 / 30	20 cycles / N/A	(Huang, 2022)
WO ₃ - H ₂ Ti ₃ O ₄	NRs-NTs	RT	200	5.25	20 / 40	5 cycles / 70 days	(Rajbhar, 2022)
Co ₃ O ₄	NWs	450	100	2.32	480 / 1240	3 cycles / 20 days	(Kumarage, 2023)
Pd@In ₂ O ₃	NFs	RT	10000	293	12 / 23	5 cycles / 28 days	(Chen, 2022)

Outlook

Nanostructures with one-dimensional features, such as nanowires, nanorods, nanobelts, and nanofibers, have become important in chemical sensing. They have attracted considerable attention because of their ability to improve sensing capabilities. The existing literature primarily focuses on gas sensors that employ p-type MOXs semiconductors, which is an area that is still in the process of development. Gas sensors that use individual one-dimensional MOXs semiconductors which are especially notable for their ability to utilise the self-heating effect, offer a way to reduce power consumption in the final device. Nevertheless, the complexities inherent in nanoscale operations provide hurdles in the isolation and characterisation of individual nanowires, requiring more research and development endeavours. The possible integration of one-dimensional nanostructures to develop heterostructures with various morphologies shows potential for providing innovative methods to improve chemical sensing capabilities and address existing challenges.

Conclusion

In recent years, there has been a significant focus on using Metal Oxide Nanowires (MOX NWs), Nanorods (NRs), Nanotubes (NTs), oxide materials, and their derivatives to drive progress in the development of advanced and high-performance hydrogen (H₂) gas detecting systems. The manufacturing of MOXs nanostructures has mostly utilised hydrothermal, solvothermal, and electrospinning methods because of their cost-effectiveness and high production yields. Significantly, there is a dearth of thorough literature studies on the single-step development of MOXs, specifically focusing on in-situ growth techniques or one-pot growth approaches. Simultaneously, thoroughly examining adjustable development factors is crucial to maximising the exploitation of these structures to their total capacity. Nevertheless, ornamentation, functionalisation, and doping procedures have greatly enhanced the chemo-physical characteristics of Metal Oxides (MOXs) compared to their inherent structures.

Gas sensors for hydrogen (H₂), which function at ambient and relatively low working temperatures, have been created using one-dimensional metal oxide semiconductors (1D MOXs). Future studies should thoroughly investigate the operational processes of the described nanocomposites to assess the structural and morphological effects of each constituent material in the hybrid system. This

investigation aims to determine the best combination of components that promotes the accurate identification of substances. Therefore, this research holds significant potential for enhancing the production of high-performance sensor devices.

References

- Anusiya, G., & Jaiganesh, R. (2022). A review of fabrication methods of nanofibers and a special focus on the application of cellulose nanofibers. *Carbohydrate Polymer Technologies and Applications*, 4, 100262. <https://doi.org/10.1016/j.carpta.2022.100262>
- Brattain, W. H., & Bardeen, J. (1953). Surface properties of Germanium. *Bell System Technical Journal*, 32(1), 1–41. <https://doi.org/10.1002/j.1538-7305.1953.tb01420.x>
- Catto, A. C., Bernardini, S., Aguir, K., Longo, E., & da Silva, L. F. (2023). In-situ hydrothermal synthesis of oriented hematite nanorods for sub-ppm level detection of Ozone Gas. *Journal of Alloys and Compounds*, 947, 169444. <https://doi.org/10.1016/j.jallcom.2023.169444>
- Chen, C., Chen, W., Liu, Q., Liu, Y., Xiao, G., Chen, C., Li, F., & Zhou, J. (2022). Electrospinning of Pd-In₂O₃ nanofibers for high-performance room temperature hydrogen sensors. *ACS Applied Nano Materials*, 5(9), 12646–12655. <https://doi.org/10.1021/acsnm.2c02436>
- Chen, S.-S., Chen, X.-X., Yang, T.-Y., Chen, L., Guo, Z., & Huang, X.-J. (2024). Temperature-modulated sensing characteristics of ultrafine au nanoparticle-loaded porous zno nanobelts for identification and determination of BTEX. *Journal of Hazardous Materials*, p. 463, 132940. <https://doi.org/10.1016/j.jhazmat.2023.132940>
- Crowl, D. A., & Jo, Y.-D. (2007). The hazards and risks of hydrogen. *Journal of Loss Prevention in the Process Industries*, 20(2), 158–164. <https://doi.org/10.1016/j.jlp.2007.02.002>
- Fioravanti, A., Morandi, S., Pedrazzo, A. R., Ceccone, C., Manzoli, M., Zanetti, M., Bracco, P., Mazzocchi, M., Lettieri, S., Marani, P., & Carotta, M. C. (2022). Investigation of the key parameters for gas sensing through comparison of electrospun and sol-gel semiconducting oxides. *Ceramics International*, 48(14), 20948–20960. <https://doi.org/10.1016/j.ceramint.2022.04.087>
- Galstyan, V., Moumen, A., Kumarage, G. W. C., & Comini, E. (2022). Progress towards chemical gas sensors: Nanowires and 2D semiconductors. *Sensors and Actuators B: Chemical*, p. 357, 131466. <https://doi.org/10.1016/j.snb.2022.131466>
- Huang, B.-R., Saravanan, A., Kathiravan, D., Chiang, T.-Y., & Yang, W.-L. (2022). Growth of graphitic carbon nitride-incorporated ZnO Nanorods on silicon pyramidal substrates for enhanced hydrogen sensing applications. *ACS Applied Materials & Interfaces*, 14(36), 41481–41488. <https://doi.org/10.1021/acsnm.2c06291>
- Kaur, N., Singh, M., Casotto, A., Sangaletti, L., & Comini, E. (2023). Self-assembled monolayer functionalised NiO nanowires: Strategy to enhance the sensing performance of P-type metal oxide. *Chemical Communications*, 59(10), 1329–1332. <https://doi.org/10.1039/d2cc06530d>
- Kaur, N., Zappa, D., Ferroni, M., Poli, N., Campanini, M., Negrea, R., & Comini, E. (2018). Branch-like NiO/ZnO heterostructures for VOC sensing. *Sensors and Actuators B: Chemical*, 262, 477–485. <https://doi.org/10.1016/j.snb.2018.02.042>
- Krishna, K. G., Parne, S., Pothukanuri, N., Kathirvelu, V., Gandi, S., & Joshi, D. (2022). Nanostructured metal oxide semiconductor-based gas sensors: A comprehensive review. *Sensors and Actuators A: Physical*, p. 341, 113578. <https://doi.org/10.1016/j.sna.2022.113578>
- Kumar, A., Chen, K., Thundat, T., & Swihart, M. T. (2023). Paper-based hydrogen sensors using Ultrathin Palladium nanowires. *ACS Applied Materials & Interfaces*, 15(4), 5439–5448. <https://doi.org/10.1021/acsnm.2c18825>
- Kumar, S., Pavelyev, V., Mishra, P., Tripathi, N., Sharma, P., & Calle, F. (2020). A review on 2D

- transition metal di-chalcogenides and metal oxide nanostructures based NO₂ Gas Sensors. *Materials Science in Semiconductor Processing*, p. 107, 104865. <https://doi.org/10.1016/j.mssp.2019.104865>
- Kumarage, G. W. C., & Comini, E. (2023). Conductometric Gas Sensors. *Encyclopedia of Materials: Electronics*, pp. 564–580. <https://doi.org/10.1016/b978-0-12-819728-8.00060-7>
- Kumarage, G. W., & Comini, E. (2021). Low-dimensional nanostructures based on cobalt oxide (Co₃O₄) in chemical-gas sensing. *Chemosensors*, 9(8), 197. <https://doi.org/10.3390/chemosensors9080197>
- Kumarage, G. W., Hakkoum, H., & Comini, E. (2023). Recent advancements in TiO₂ nanostructures: Sustainable synthesis and Gas Sensing. *Nanomaterials*, 13(8), 1424. <https://doi.org/10.3390/nano13081424>
- Kumarage, G. W., Panamaldeniya, S. A., Maddumage, D. C., Moumen, A., Maraloiu, V. A., Mihalcea, C. G., Negrea, R. F., Dassanayake, B. S., Gunawardhana, N., Zappa, D., Galstyan, V., & Comini, E. (2023). Synthesis of TiO₂-(B) nanobelts for acetone sensing. *Sensors*, 23(19), 8322. <https://doi.org/10.3390/s23198322>
- Kumarage, G. W., Zappa, D., Mihalcea, C. G., Maraloiu, V.-A., Stefan, M., & Comini, E. (2023). Revolutionizing N-Type Co₃O₄ nanowire for Hydrogen Gas Sensing. *Advanced Energy and Sustainability Research*, 4(10). <https://doi.org/10.1002/aesr.202300067>
- Liang, Y., Sun, S., Deng, T., Ding, H., Chen, W., & Chen, Y. (2018). The preparation of tio2 film by the sol-gel method and evaluation of its self-cleaning property. *Materials*, 11(3), 450. <https://doi.org/10.3390/ma11030450>
- Lu, S., Zhang, Y., Liu, J., Li, H.-Y., Hu, Z., Luo, X., Gao, N., Zhang, B., Jiang, J., Zhong, A., Luo, J., & Liu, H. (2021). Sensitive H₂ gas sensors based on SnO₂ nanowires. *Sensors and Actuators B: Chemical*, p. 345, 130334. <https://doi.org/10.1016/j.snb.2021.130334>
- Lupan, C., Mishra, A. K., Wolff, N., Drewes, J., Krüger, H., Vahl, A., Lupan, O., Pauporté, T., Viana, B., Kienle, L., Adelung, R., de Leeuw, N. H., & Hansen, S. (2022). Nanosensors based on a single zno: Eu nanowire for Hydrogen Gas Sensing. *ACS Applied Materials & Interfaces*, 14(36), 41196–41207. <https://doi.org/10.1021/acsmi.2c10975>
- Lv, Q., Li, R., Qu, Y., Yu, M., Zhang, L., & Li, H. (2023). CEO nanorods decorated In₂O₃ nanoparticles for enhanced low-temperature detection of hydrogen. *Inorganic Chemistry Communications*, 158, 111474. <https://doi.org/10.1016/j.inoche.2023.111474>
- Mijatovic, D., Eijkel, J. C., & van den Berg, A. (2005). Technologies for nanofluidic systems: Top-down vs. bottom-up—a review. *Lab on a Chip*, 5(5), 492. <https://doi.org/10.1039/b416951d>
- Moumen, A., Kumarage, G. C., & Comini, E. (2022). P-type metal oxide semiconductor thin films: Synthesis and chemical sensor applications. *Sensors*, 22(4), 1359. <https://doi.org/10.3390/s22041359>
- Patil, V. L., Bhosale, S. R., Bhosale, R. R., Tarwal, N. L., Vanalakar, S. A., Dhavale, R. P., Sharma, K. K., & Patil, P. S. (2023). Low-temperature chemiresistive gas sensing performance towards oxidising gas based on chemically prepared Ga-doped ZnO nanorods. *Inorganic Chemistry Communications*, 152, 110691. <https://doi.org/10.1016/j.inoche.2023.110691>
- Punginsang, M., Zappa, D., Comini, E., Wisitorsaat, A., Sberveglieri, G., Ponzoni, A., & Liewhiran, C. (2022). Selective H₂S gas sensors based on ohmic hetero-interface of au-functionalized WO₃ nanowires. *Applied Surface Science*, 571, 151262. <https://doi.org/10.1016/j.apsusc.2021.151262>
- Rajbhar, M. K., Das, P., Möller, W., & Chatterjee, S. (2022). Core–shell nanostructures of tungsten oxide and hydrogen titanate for H₂ gas adsorption. *ACS Applied Nano Materials*, 6(1), 212–227. <https://doi.org/10.1021/acsnm.2c04268>
- Şennik, E., Alev, O., & Öztürk, Z. Z. (2016). The effect of PD on the H₂ and VOC sensing properties

- of TiO₂ Nanorods. *Sensors and Actuators B: Chemical*, 229, 692–700. <https://doi.org/10.1016/j.snb.2016.01.089>
- Shi, Y., Xu, H., Liu, T., Zeb, S., Nie, Y., Zhao, Y., Qin, C., & Jiang, X. (2021). Advanced development of metal oxide nanomaterials for H₂ gas sensing applications. *Materials Advances*, 2(5), 1530–1569. <https://doi.org/10.1039/d0ma00880j>
- Shrisha, Wu, C.-M., Motora, K. G., Chen, G.-Y., Chu, J. P., Cheng, Y., & Hsu, H.-H. (2023). Development of P-type zinc oxide nanorods on zirconium-based metallic glass nanotube arrays by facile hydrothermal method for gas sensing applications. *Chemical Engineering Journal*, p. 463, 142381. <https://doi.org/10.1016/j.cej.2023.142381>
- Sisman, O., Zappa, D., Maraloiu, V.-A., & Comini, E. (2023). Fabrication of cuo (p)–zno (n) core–shell nanowires and their H₂-sensing properties. *Materials*, 16(13), 4802. <https://doi.org/10.3390/ma16134802>
- Sun, X., Gao, R., Wu, Y., Zhang, X., Cheng, X., Gao, S., Xu, Y., & Huo, L. (2023). Novel in-situ deposited V₂O₅ nanorods array film sensor with enhanced gas sensing performance to N-Butylamine. *Chemical Engineering Journal*, p. 459, 141505. <https://doi.org/10.1016/j.cej.2023.141505>
- Sztaberek, L., Mabey, H., Beatrez, W., Lore, C., Santulli, A. C., & Koenigsmann, C. (2019). Sol–gel synthesis of ruthenium oxide nanowires to enhance methanol oxidation in supported platinum nanoparticle catalysts. *ACS Omega*, 4(10), 14226–14233. <https://doi.org/10.1021/acsomega.9b01489>
- Tan, Y., & Zhang, J. (2023). Highly sensitive ethanol gas sensors based on co-doped SNO₂ nanobelts and pure SnO₂ nanobelts. *Physica E: Low-Dimensional Systems and Nanostructures*, p. 147, 115604. <https://doi.org/10.1016/j.physe.2022.115604>
- Tasyurek, L. B., Isik, E., Isik, I., & Kilinc, N. (2023). Enhancing the performance of tio₂ nanotube-based hydrogen sensors through crystal structure and Metal Electrode. *International Journal of Hydrogen Energy*. <https://doi.org/10.1016/j.ijhydene.2023.08.202>
- Wang, D., Han, C., Zheng, C., Fang, H., Xu, D., & Zhao, H. (2023). Fabrication of a ppb-level NO₂ gas sensor by sensitising nanobundles assembled by In₂O₃ nanotubes with TiO₂ quantum dots. *Sensors and Actuators B: Chemical*, p. 387, 133833. <https://doi.org/10.1016/j.snb.2023.133833>
- Xu, J., He, X., Xu, K., Liao, H., & Zhang, C. (2023). Synthesis and optimisation strategies of nanostructured metal oxides for chemiresistive methanol sensors. *Ceramics International*, 49(13), 21113–21132. <https://doi.org/10.1016/j.ceramint.2023.03.274>
- Yang, B., Myung, N. V., & Tran, T. (2021). 1D metal oxide semiconductor materials for Chemiresistive Gas Sensors: A Review. *Advanced Electronic Materials*, 7(9). <https://doi.org/10.1002/aelm.202100271>
- Yusof, N. M., Rozali, S., Ibrahim, S., & Siddick, S. Z. (2023). Synthesis of hybridised fireworks-like go-co₃o₄ nanorods for acetone gas sensing applications. *Materials Today Communications*, p. 35, 105516. <https://doi.org/10.1016/j.mtcomm.2023.105516>
- Zakharova, G. S., Liu, Y., Enyashin, A. N., Yang, X., Zhou, J., Jin, W., & Chen, W. (2018). Metal cations doped vanadium oxide nanotubes: Synthesis, electronic structure, and gas sensing properties. *Sensors and Actuators B: Chemical*, pp. 256, 1021–1029. <https://doi.org/10.1016/j.snb.2017.10.042>