

SnO₂-BASED CO SENSORS: RECENT ADVANCES AND FUTURE DIRECTIONS

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SnO₂-based CO sensors have garnered significant attention due to their remarkable potential in gas sensing applications. This review paper presents a comprehensive analysis of the recent advances and future directions in SnO₂-based CO sensor development. A detailed examination of various synthesis methods, nanostructured designs, and innovative strategies to enhance the sensitivity and selectivity is provided. The study highlights the pivotal role of advanced fabrication techniques, such as quasi-molecular imprinting and doping with noble metals in improving sensor performance. A comparative analysis with other metal oxide-based sensors, including ZnO, In₂O₃, and WO₃, elucidates on SnO₂'s advantages in terms of the sensitivity and stability. However, challenges including the manufacturing complexity, scalability, stability, and cross-sensitivity are addressed, emphasising the need for continued research in these areas. The review also underscores the potential of AI and ML integration for enhanced sensor performance and real-time data analysis. The paper concludes by outlining future directions, including the exploration of hierarchical and composite structures, advancements in catalysts and dopants, scalable manufacturing processes, and applications in various sectors such as healthcare, industrial automation, and environmental monitoring.

INTRODUCTION

Tin dioxide, or stannic oxide, represented by the chemical formula SnO₂, is a compound that has been gaining attention in the field of gas sensing, owing to its unique set of properties. There are three distinct crystal forms of SnO₂: tetragonal, hexagonal, and orthogonal. However, the latter two, hexagonal and orthogonal, exist only under high temperature and pressure conditions [1]. SnO₂ is widely recognised as a quintessential n-type semiconductor material due to its tetragonal crystal structure. At room temperature, it adopts the rutile structure and exhibits a band gap within the range of 3.5 – 4.0 eV. The crystal space group of SnO₂ is P4₂/mm (No.136), and its lattice constants are represented as $a = 4.737 \text{ \AA}$ and $c = 3.186 \text{ \AA}$ [2]. In its original cell structure, the SnO₂ crystal consists of a combination of two Sn atoms and four O atoms, as visually depicted in Figure 1A. In the bulk phase, Sn atoms occupy both vertex and body centre positions within the tetragonal body. The Sn atoms located at

the body centre form bonds with the six surrounding O atoms, creating a coordination environment reminiscent of a regular octahedron. The stoichiometric ratio between the Sn atoms and O atoms is 1:2 [3]. Each crystal phase encompasses various crystal planes, broadly categorised as high-index and low-index crystal planes. These distinct crystal facets exhibit varying stabilisation energies and diverse gas adsorption capabilities.

The properties that make SnO₂ attractive for sensing applications include its high sensitivity to gas species, excellent thermal stability, and ease of fabrication into various nanostructures [4–7]. Its sensitivity to gas species can be attributed to its surface reactions with gases, such as CO. Upon exposure to CO, the surface of SnO₂ undergoes a change in electrical resistance, a phenomenon that can be harnessed for sensing purposes. The thermal stability of SnO₂ ensures that it can operate in a variety of environmental conditions without a significant loss in performance. Furthermore, the possibility of synthesising SnO₂ into different nanostructures, such as nanoparticles, nanowires, and

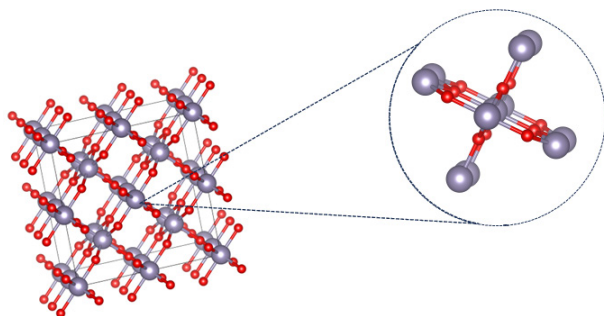


Figure 1. $2 \times 2 \times 2$ structure of SnO₂.

nanorods, opens up avenues for enhancing its sensitivity and selectivity [8]. These nanostructures increase the surface area available for interaction with gas molecules, thereby boosting the sensor's performance.

CO detection is a critical application where SnO₂ has found a foothold. Its strong interaction with CO molecules and its ability to respond quickly to changes in CO concentrations have made it a material of choice for CO sensor development [9]. Furthermore, the option to modify SnO₂'s surface with dopants or catalysts offers opportunities to tailor the sensor's performance specifically for CO detection. The understanding of SnO₂'s working principles in CO sensing relies on its surface chemistry. When CO molecules are adsorbed onto the SnO₂ surface, they react with the adsorbed oxygen species, triggering a change in the electrical resistance. This change can be correlated to the concentration of CO in the environment, providing a measure of the gas' presence [10]. Continued research into the fabrication, modification, and application of SnO₂ has led to advancements that enable more accurate and efficient CO detection. Its role in miniaturised and portable sensors is particularly significant, given the growing demand for user-friendly and accessible sensing solutions [11].

CO is an insidious environmental hazard. A product of incomplete combustion, it is a colourless, odourless, and tasteless gas, which allows it to go undetected without the help of specialised sensing equipment. The dangers associated with CO exposure are manifold. In low concentrations, it can cause mild symptoms such as headaches, dizziness, nausea, and fatigue, which are often mistaken for other common illnesses [12]. However, in higher concentrations, it can lead to more severe symptoms like confusion, loss of consciousness, and in extreme cases, it can be fatal. The ability of CO to bind to haemoglobin — the molecule responsible for oxygen transport in the blood — is at the root of its harmful effects. When CO is inhaled, it forms carboxyhaemoglobin, which prevents haemoglobin from carrying oxygen [13]. As a result, vital organs like the heart and brain that require large amounts of oxygen can be starved, leading to serious health issues. Furthermore,

long-term exposure to even relatively low concentrations of CO can lead to chronic health problems. For example, chronic obstructive pulmonary disease and ischemic heart disease have been linked to long-term CO exposure [14]. This silent threat necessitates the development of efficient and reliable CO detection technologies.

Detecting CO accurately and reliably is, therefore, of paramount importance, and it is here that SnO₂-based sensors play a crucial role. The unique sensing characteristics of SnO₂ — its high sensitivity and selectivity towards CO — make it a suitable candidate for CO sensor development. Early detection of CO allows for the implementation of measures to limit exposure and avert any potential harm. This is particularly important in environments where CO production is likely, such as homes with gas stoves or heaters, industrial settings, and urban areas with high traffic [15]. An efficient CO sensor should not only be able to detect the gas at low concentrations, but also be selective — i.e., it should not produce false alarms due to interference from other gases. Furthermore, the sensor should provide quick response and recovery times to ensure real-time monitoring. With advancements in SnO₂-based sensor technologies, achieving these objectives has become increasingly possible [16]. The manipulation of SnO₂ at the nano-level, as well as the introduction of catalysts and dopants, has allowed for improvements in both sensitivity and selectivity.

As we advance into an era where the importance of environmental monitoring is realised and prioritised, the role of efficient gas sensing technologies becomes critical. Given the unique characteristics and evolving adaptations of SnO₂ in the field of gas sensing, this review aims to provide a comprehensive overview of the progress in SnO₂-based CO sensors. We explored the journey from traditional SnO₂-based sensors to the most recent advancements, comparing them with other gas sensors, and examining the challenges that are currently being addressed in this field. Furthermore, we aim to peek into the future, envisaging the potential improvements and application areas for these sensors. In doing so, we underlined the significance of SnO₂ in the realm of CO sensing and stimulate further research and development efforts to harness its full potential. This review is aimed at researchers, academicians, industry professionals, and anyone interested in the ongoing evolution of gas sensing technologies. The ultimate objective is to contribute to the enhancement of safety and well-being by promoting a better understanding and development of CO detection technologies.

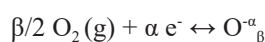
RESULTS AND DISCUSSION

Basic Working Principle of SnO₂-based CO Sensors

The comprehensive exploration of the fundamental gas sensing mechanisms of SnO₂ remains an ongoing endeavour. Nonetheless, the operational foundation of SnO₂-based sensors hinges upon the detection of alterations in the electrical conductivity exhibited by n-type materials when surface-chemisorbed oxygen interacts with reducing gases, such as CO. Simplistically put, in an uncontaminated air environment, the conductivity of SnO₂ remains limited due to the confinement of conduction electrons to the surface oxygen. In contrast, the introduction of a reducing gas leads to the liberation of electrons from the surface states, resulting in heightened conductivity. Consequently, the adsorption of gaseous entities manages the surface resistance of SnO₂.

Given that the gas sensing attributes of SnO₂ revolve around the chemisorption of gas molecules on its surface, acquiring an in-depth comprehension of the charge transfer intrinsic to chemisorption processes holds paramount importance. For a more detailed exploration of this facet, interested readers can delve into a comprehensive review available in the literature [17]. Here, a succinct overview is provided.

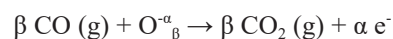
In ambient air, the band structures of SnO₂ undergo modification upon the adsorption of oxygen molecules. This surface interaction disrupts the regularity of the crystal structure, giving rise to unsaturated sites or dangling bonds. In the specific instance of an oxygen molecule, it acquires electrons from the SnO₂ surface, facilitating a charge transfer scenario that can be expressed through the following equation:



In the context of different oxygen reduction states, the parameter α can assume values of 1 or 2. For single atom/ionic forms of oxygen, α is set to 1, while for the molecular form of oxygen, α takes on a value of 2.

The interaction involving charge transfer between atmospheric oxygen and the SnO₂ surface has a consequential outcome: the creation of a space charged layer at the surface. This accumulated charge on the surface generates an electric field, resulting in the deformation of the energy bands within SnO₂. Specifically, a negatively charged surface leads to an upward bending of the bands. This phenomenon pushes the Fermi levels into the band gap of SnO₂. Consequently, it reduces the concentration of charge carriers, inducing an electron depletion region. In essence, this process entails the entrapment of electrons at the surface, consequently augmenting the electrical resistance (or diminishing the conductivity) of the surface layer.

Upon adsorption of a reducing molecular gas on the surface, electrons can be transferred to these molecules. This exchange occurs when the lowest unoccupied molecular orbitals (LUMOs) of the adsorbate are situated below the acceptor levels (Fermi levels) of SnO₂. Conversely, electrons are donated to SnO₂ when the highest occupied molecular orbitals (HOMOs) of the adsorbate lie above the Fermi levels of SnO₂, representing donor levels. For instance, in the case of a reducing gas like CO, the reaction with adsorbed oxygen leads to the formation of CO₂.



In this reaction, the liberated electrons are introduced into the conduction band of SnO₂. This phenomenon leads to a notable reduction in electrical resistance, consequently resulting in enhanced conductivity. The schematic representation of the formation and reduction of the depletion region through the adsorption of oxygen and a reducing gas is depicted in Figure 2.

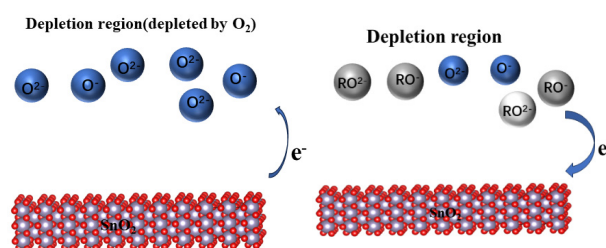


Figure 2. Oxygen extract electrons from metal oxide thereby decreasing the conductivity, and when a reducing agent (R) is present, electrons are injected into the oxide again and, thus, increase the conductivity.

The variation in Fermi level of nano-scale SnO₂ powder sensors upon exposure to elevated temperatures and gases, O₂ and CH₄, has been explored through X-ray photoelectron spectroscopy (XPS) [18]. In Figure 3, the alterations in the binding energy (BE) for Sn 3d_{5/2} and O 1s core levels are depicted concerning the exposure duration to different temperatures (120 °C and 250 °C) and gases (O₂ and CH₄). For instance, exposure to O₂ at 120 °C resulted in a 0.2 eV upward band bending. Conversely, subsequent exposure to CH₄ induced a 0.1 eV downward band bending, as expected due to the oxidative and reducing properties of the respective gases. Analogous variations in surface band bending were evident at 250 °C, although the quantitative analysis suggests an augmentation in oxygen absorption. These outcomes unequivocally underscore the gas sensing mechanism's electronic nature. Notably, in photoemission measurements, where both the sample and analyser are grounded, the substrate's Fermi level

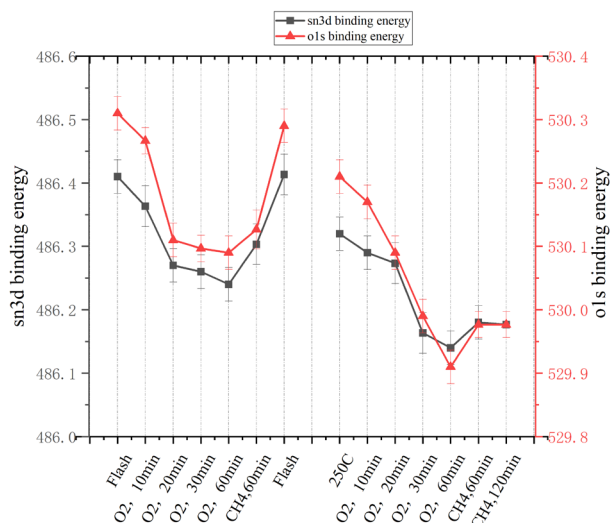


Figure 3. Evolution of the Sn 3d_{5/2} and O 1s core levels BE as a function of the surface treatment and scanning temperature. The surface treatments prior to each scan are given on the x-axis, while the scanning temperatures are indicated on the top of the graph.

consistently appears at a fixed position. The downward shift in Fermi level (relative to the vacuum level) caused by the band bending leads to corresponding downward shifts in Sn 3d_{5/2} and O 1s core levels' binding energies [19].

Historical Perspective: Evolution and Improvements over the Years

The concept of gas detection using semiconducting materials began to take shape in the mid-20th century. The recognition of the interaction between gas molecules and the surface of semiconducting materials led to the exploration of these materials as potential gas sensors. Among them, SnO₂ emerged as a promising candidate for CO sensing due to its strong affinity towards oxygen and its high electron mobility.

The first generation of SnO₂-based CO sensors, developed in the 1970s and 1980s, were constructed as simple pellets or thick films [20, 21]. The sensing material was compressed or deposited onto a substrate, often with heating elements to maintain the necessary operating temperature. These devices relied on the bulk properties of SnO₂ and, while effective for their time, had several limitations, including a lack of selectivity, long response and recovery times, and high power consumption due to the need for constant heating [22].

In the 1980s and 1990s, advancements in material science and fabrication techniques led to the development of thin-film SnO₂ sensors. By reducing the thickness of the SnO₂ layer, the sensor's performance was significantly improved, with faster response and recovery times, better sensitivity, and lower power consumption [23]. These sensors were often fabricated

using techniques such as sputtering or chemical vapour deposition (CVD), allowing for the more precise control over the sensor's properties [24].

However, the quest for improved sensitivity and selectivity led researchers to explore the potential of SnO₂ at the nano-scale. The turn of the 21st century saw the rise of SnO₂ nanostructures in gas sensing. By controlling the shape, size, and morphology of the SnO₂ structures at the nanometre scale, researchers were able to enhance the sensor's performance even further [25]. Nano-sized SnO₂ particles provide a larger surface area for gas adsorption, leading to increased sensitivity. Meanwhile, the use of different nanostructures (e.g., nanowires, nanotubes, nanorods) allowed for improved control over the sensor's properties, further enhancing its performance. For example, Wang and colleagues [26] investigated the detection of CO gas at room temperature using polycrystalline SnO₂ nanowires. In their study, they employed a synthesis approach involving the combination of SnC₂O₄·2H₂O with poly(vinylpyrrolidone) in ethylene glycol, followed by refluxing at 195 °C for 3 hours. These SnO₂ nanowires exhibited the ability to detect CO gas at a concentration as low as 20 ppm, with a sensor response of 4 %. In a separate study, Fisher et al. [27] introduced a gas sensor for CO detection based on tin oxide nanowires. Their approach involved plasma treatment using Ar/O₂ and H₂O. This innovative material was synthesised through chemical vapour deposition.

These advancements have been paralleled by progress in the understanding of the sensor's working mechanism and the factors influencing its performance. Studies into the role of the operating temperature, the effects of surface modification with dopants or catalysts, and the influence of environmental conditions have all contributed to the ongoing improvement in SnO₂-based CO sensors [28]. Diverse additives, including metals like Ag, Au, Pd, Pt, and various metal oxides, play a pivotal role in augmenting the sensing properties, which encompass sensitivity, response time, and reproducibility, tailored for specific gases [29, 30]. The efficacy of these additives stems from their ability to either elevate the concentration of reactants at the surface or diminish the activation energy required for the reactions, and sometimes accomplishing both simultaneously. The impact of these additives on the surface of metal oxides is explicated through three distinct models: 1) Catalytic effect; 2) Spill-over effect; and 3) Fermi energy control. These models presuppose the presence of metal or metal oxide additives on the sensing oxide surface, manifesting as dispersed clusters. Moreover, beyond these surface-supported clusters, it is imperative to consider the bulk doping of metal oxides via additives, particularly notable in the cases of Pd and Pt. In such scenarios, Pd and Pt are conjectured to function as either bulk acceptor-type or donor-type dopants.

From the humble beginnings of pellet and thick film sensors to the current state-of-the-art nanostructured sensors, the journey of SnO₂-based CO sensors has been marked by continuous evolution and refinement. The advancements made over the years have been driven by the quest for better performance – increased sensitivity, improved selectivity, faster response and recovery, and lower power consumption.

Examples of Advanced SnO₂-based CO Sensors

The study by Li et al. [31] presents a novel approach to enhance the performance of CO gas sensors based on SnO₂NPs. The researchers utilised a quasi-molecular-imprinting mechanism during the device fabrication, which involved exposing one group of sensors (SC) to CO gas during drying, while another group (SA) was dried in air for comparison (Figure 4A). The results demonstrated that the SC sensors exhibited both quicker response times and higher sensitivity compared to SA sensors (Figure 4B). Notably, the response of SC sensors to 500 ppm CO gas was 2.1 times higher, and they displayed shorter response and recovery times. The study also confirmed a detection limit of around 5 ppm and showed that the molecular imprinting technique significantly improved the adsorption and desorption performance of CO gas. Overall, the incorporation of quasi-molecular-imprinting during fabrication notably enhanced the CO gas sensors' sensitivity and response kinetics, showcasing potential for novel gas sensing applications.

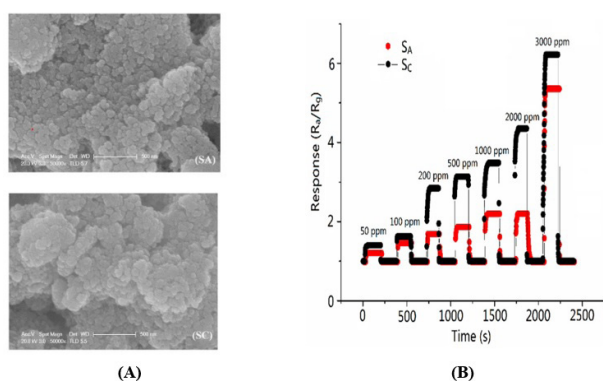


Figure 4. (A) SEM images of SA and SC sensors. (B) Responses to 50, 100, 200, 500, 1000, 2000, 3000 ppm of CO gas for SA and SC at 300 °C. Reproduced with permission from Ref. [31].

Doping noble metals can be used for enhancing CO sensitivity and selectivity. Bahrami et al. [32] investigated the impact of incorporating AuNPs into SnO₂ gas sensors on their sensitivity and selectivity to CO in the presence of propane and methane. By employing a co-precipitation method, AuNPs were integrated into the SnO₂ matrix. The results revealed that the Au/SnO₂

sensors exhibited significantly higher sensitivity towards CO than SnO₂ sensors, with a response that increased with the concentration. The selectivity of Au/SnO₂ sensors to CO was remarkably improved, being approximately 4–17 times more selective to CO in the presence of propane and 7–20 times more selective in the presence of methane. This heightened selectivity was attributed to the catalytic properties of the gold nanoparticles, which facilitated enhanced interactions with CO and oxygen species. Zhang et al. [33] focused on the development of a microstructure gas sensor for the sensitive detection of low-level CO. Through a sol-gel method, In/Pd-doped SnO₂ is synthesised and coated onto a silicon substrate with Pt electrodes to create the sensor. Notably, the sensor exhibits remarkable performance at an operating temperature of 140 °C, demonstrating high sensitivity and selectivity to CO while having minimal cross-responses to common interfering gases. The sensor's exceptional capability to detect CO concentrations as low as 1 ppm is emphasised, with response and recovery times of around 15 and 20 seconds, respectively. Wurzing and Reinhardt investigated the CO-sensing properties of differently doped SnO₂ sensors in hydrogen-rich atmospheres relevant to fuel cell processes. Pt-doped sensors exhibited the highest sensitivity to CO at around 220 °C, while cross-sensitivities to hydrogen, carbon dioxide, and water were significantly lower. After 9 months, the sensors showed decreased sensitivity, which could be partially restored through reoxidation at 750 °C. An Fe addition to Pt-doped sensors enhanced the CO sensitivity, but reduced the selectivity. A surface analysis revealed the presence of formate, OH, and methoxy groups. The proposed mechanism involving formate intermediates explained the observed CO-sensing behaviour. Numerical simulations supported the influence of formate formation via CO on the sensor conductance. Tangirala et al. [34] also focused on the synthesis and characterisation of doped SnO₂ powders for gas sensing applications. Various doping methods and precipitation agents were employed to create Cu-, Pt-, and Pd-doped SnO₂ powders. Through SEM and High-resolution transmission electron microscopy (HRTEM) analyses, it was observed that the dopants affected the crystallite size and porosity, with Cu-doped powders exhibiting stacking faults and Pt/Pd-doped powders forming clusters. The sensing responses of these powders to CO gas were tested, revealing that Cu:SnO₂ powders showed significantly higher responses compared to Pt and Pd:SnO₂ powders. Specifically, the Cu:SnO₂ powders achieved a maximum sensing response of 1782, outperforming other variants. The observed differences in the morphology significantly influence the gas sensing performance of the doped SnO₂ powders (Figure 5). Chemical doping with urea leads to the formation of well-defined crystallites with smaller particle sizes, resulting in a mesh-like porous structure. This morphology increases the surface area and provides

more active sites for gas adsorption, enhancing the sensitivity to CO gas. On the other hand, impregnation with ammonia forms agglomerated particles, which cluster on the surface of SnO₂ crystals. These clusters act as catalytic sites, promoting chemical interactions between CO and oxygen adsorbed on the surface. This catalytic mechanism accelerates the gas reaction at lower temperatures, contributing to higher sensitivity. The face-to-face contact in the non-spherical tetragonal particles further enhances surface-depletion control, aiding in a higher sensing response.

Some other elements were also tested for enhancing the performance of SnO₂. Li et al. investigated [35] the gas-sensing capabilities of Sb, S co-doped SnO₂ (1 1 0) surfaces for CO detection using first-principles calculations. The researchers found that the adsorption of CO molecules is significantly enhanced on these doped surfaces compared to pristine SnO₂. By examining various adsorption configurations, the authors revealed that CO molecules preferentially bind to specific sites on the doped surfaces, resulting in increased adsorption energies. This binding leads to electron transfer and modifies the electronic structure, consequently boosting the surface conductivity. Specifically, the Sb, S co-doped SnO₂ surfaces exhibit the highest sensitivity to CO gas, with an improved adsorption energy of -5.82 eV.

The combination of SnO₂ with other metal oxides have also showed enhancement capabilities for CO sensing. Pourfayaz et al. [36] investigated the enhancement of ethanol detection selectivity in gas sensors using CeO₂ doped SnO₂. The researchers prepared sensors through a sol-gel method, sintering

them at different temperatures, and analysed their performance. The addition of 2.0 wt. % ceria to SnO₂ significantly improved the ethanol selectivity at specific temperatures. Notably, at 300 °C, ceria-doped sensors displayed up to 48.2 times higher ethanol selectivity compared to liquefied petroleum gas, CO, and CH₄. Furthermore, the ceria-doped sensors exhibited faster recovery times in the presence of ethanol. These findings emphasise the potential of ceria-doped SnO₂ sensors to enable highly selective ethanol detection, addressing challenges related to cross-sensitivity to other gases. Gulevich et al. [37] focused on investigating the sensor properties of nanocomposite materials comprised of SnO₂ and SiO₂ for detecting CO gas, particularly in humid air conditions. The results showed that the introduction of SiO₂ increased specific surface area, leading to enhanced chemisorbed oxygen interactions with CO. Notably, the study highlighted the CO oxidation process on the surface of SnO₂/SiO₂ nanocomposites under wet conditions, demonstrating how SiO₂ fragments preferentially adsorb water molecules, preventing the blocking of active CO interaction sites on SnO₂, thus maintaining reliable sensor performance in humid conditions (Figure 6). The calibration curves indicated power-law relationships between the sensor response and the CO concentration, providing quantitative insights into the sensor's performance. Yin et al. [38] focused on enhancing the selectivity of gas sensors by utilising SnO₂-Mn₃O₄ nanocomposites. The research reveals that the gas sensing response of these nanocomposite sensors varies based on the molar ratio of Sn to Mn. Notably, the sensor configuration demonstrates unique behaviour:

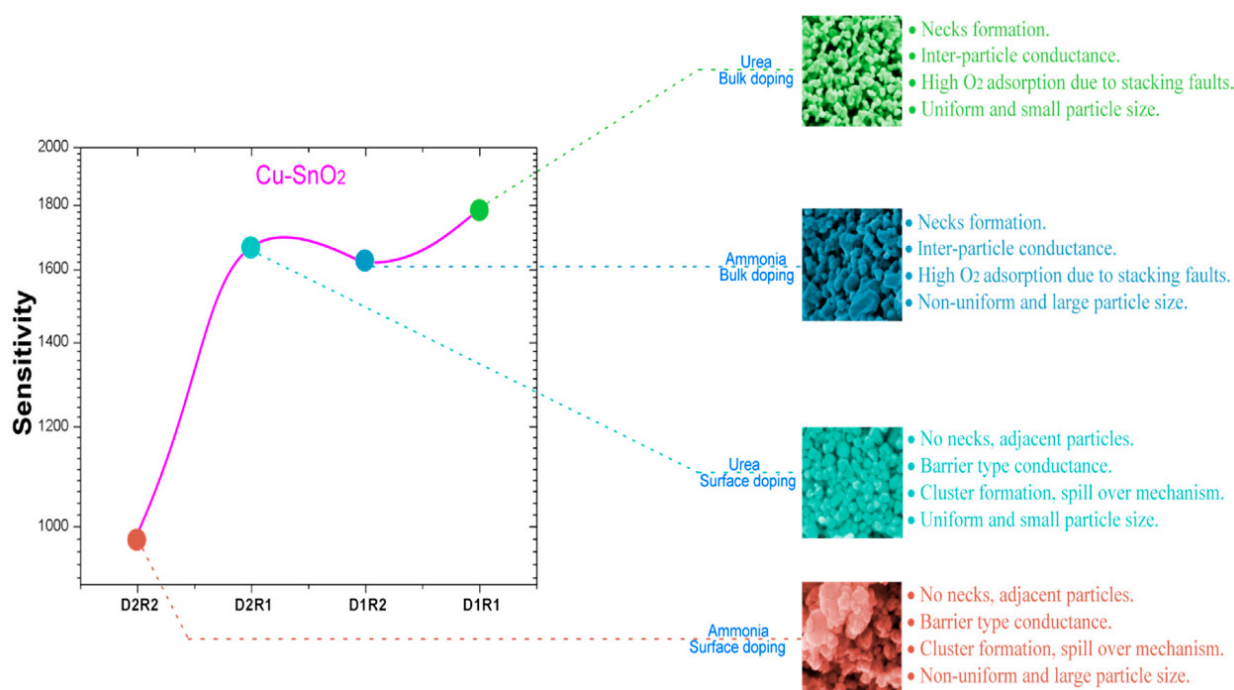


Figure 5. Graphical comparison of the synthesis methods of Cu:SnO₂ pellets with corresponding intellects for achieving the high sensing responses for higher CO concentrations (0–300 ppm). Reproduced with permission from Ref. [34].

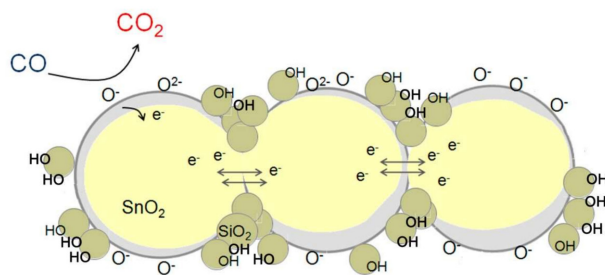


Figure 6. Schematic representation of the process of CO oxidation on the surface of an $\text{SnO}_2/\text{SiO}_2$ nanocomposite under wet conditions. Reproduced with permission from Ref. [37].

it exhibits an n-type response to CO and a p-type response to H_2 , even at a fixed testing temperature of 350 °C. The key insight lies in the formation of a p-n heterojunction, which influences the sensor's response to the gases. The study establishes that the sensor's selectivity can be adjusted by manipulating the ratio of p-type and n-type materials, presenting an innovative approach to overcoming the cross-sensitivity challenge.

The combination of SnO_2 with sulfides can also enhance the sensing performance. For example, Kim et al. [39] focused on designing a novel CO gas sensor using Au-decorated n-type SnO_2 /p-type WS_2 composites. By incorporating 10 wt. % of SnO_2 nanowires (NWs) within WS_2 nanosheets, a unique 3D sensor structure was created for improved CO sensing. The addition of SnO_2 NWs transitioned the sensor's behaviour from a p-type to an n-type, with the Au-decorated 10 wt. % SnO_2 - WS_2 composite exhibiting the highest sensitivity to CO gas. The enhanced sensor response was attributed to chemical sensitisation effects induced by the AuNPs, facilitating more efficient oxygen ionosorption and catalytic CO oxidation. This composite sensor demonstrated a

notable response to CO gas at room temperature, with its performance surpassing that of similar 2D nanostructure-based gas sensors. The proposed sensor design not only offered improved gas selectivity and response, but also demonstrated the potential for low-power consumption CO sensing under various conditions, including humid environments. Similarly, they also investigated different sensor configurations, including bare WS_2 , Au-decorated WS_2 , SnO_2 -decorated WS_2 , and Au- SnO_2 -co-decorated WS_2 [40]. The most notable outcomes include the Au- SnO_2 -co-decorated WS_2 sensor exhibiting the highest response (3.687) to 50 ppm CO gas at an optimal voltage of 4.7 V, showcasing enhanced selectivity and sensitivity. The sensor retained reliable performance under bending, tilting, and stretching, with consistent response after thousands of cycles. Humidity affected the sensor performance, with a higher humidity reducing the CO response due to increased water molecule adsorption. The Au- SnO_2 -co-decorated WS_2 sensor demonstrated the ability to detect low CO concentrations and maintained repeatability over multiple cycles. The research highlights the pivotal role of Schottky junctions, heterojunctions, and catalytic properties in augmenting the gas sensing performance of WS_2 nanosheets, underscoring their potential for low-power, flexible, and efficient gas sensing applications.

The addition of a polymer into the SnO_2 can also enhance the sensing performance towards CO. Jian et al. [41] focused on developing CO sensors using sol-gel synthesised SnO_2 NPs combined with polyaniline (PANI) deposition. These sensors exhibited enhanced performance, particularly at lower operating temperatures. The SnO_2 NPs, characterised by their small size of 5-9 nm, were screen-printed onto substrates and demonstrated good stability even after heat treatment (Figure 7). PANI deposition led to nanoparticle agglomeration

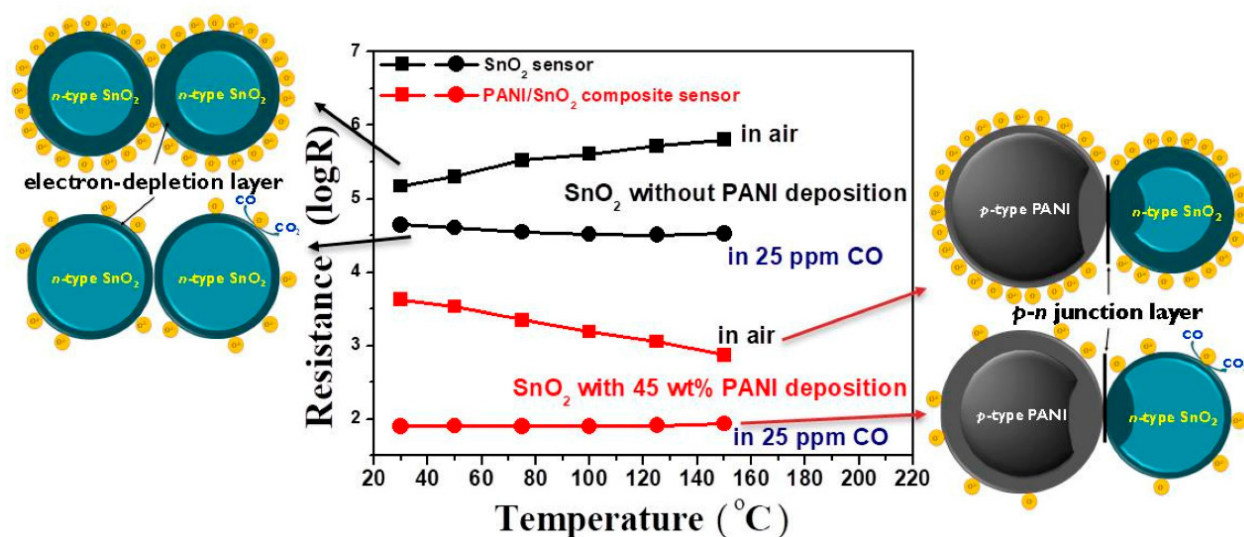


Figure 7. Resistance of the SnO_2 powder coatings without and with 45 wt. % PANI deposition as a function of operating temperature under air and 25 ppm CO [41].

meration and a porous structure, enhancing the resistance difference between the air and CO gas. The resulting sensors displayed remarkable sensitivity, with PANI-deposited SnO₂ sensors showing responses ranging from approximately 40 to 70 to varying CO concentrations (25-200 ppm) at temperatures between 30 and 50 °C. This superior performance, coupled with good reversibility and stability, suggests that these composite sensors hold promise for practical carbon monoxide detection applications.

Comparative Analysis of SnO₂-based CO Sensors with Other Gas Sensors

One of the most practical ways to understand and appreciate the utility and efficacy of SnO₂-based CO sensors is to compare them with other metal-oxide-based sensors. Here, we focused on a comparative analysis with ZnO, In₂O₃, and WO₃, which have also been widely studied for gas sensing applications. Among the four metal-oxides discussed here, SnO₂-based sensors have shown impressive results in terms of sensitivity, particularly towards reducing gases like CO. The high sensitivity of SnO₂ sensors can be attributed to their large surface-to-volume ratio (especially in nanostructured forms) and the strong interaction between SnO₂ and oxygen, which enhances the adsorption and subsequent reaction with CO [42]. ZnO, on the other hand, exhibits a slightly lower sensitivity towards CO. This could be attributed to the lower number of active oxygen species on its surface, which results in less interaction with CO [43]. Nevertheless, ZnO has shown excellent sensitivity towards other gases like H₂ and NO₂, which highlights its potential for multi-gas detection applications. In₂O₃, similar to SnO₂, exhibits good sensitivity towards CO [44]. However, In₂O₃ sensors often require higher operating temperatures to achieve this sensitivity, which may pose challenges for certain applications [45]. WO₃ sensors have demonstrated a broad range of sensitivity towards various gases, but their sensitivity towards CO is relatively lower than that of SnO₂ [46]. The difference in sensitivity between these metal-oxide sensors can often be attributed to the differences in their material properties, such as bandgap energy, charge carrier concentration, and crystal structure.

In terms of selectivity, SnO₂-based CO sensors have shown decent performance, but their selectivity can be compromised when exposed to other reducing gases. This is an area where some other metal-oxides, particularly WO₃, have an edge [47]. WO₃ has demonstrated good selectivity towards NO₂, even in the presence of other gases. In₂O₃ and ZnO sensors, similar to SnO₂ sensors, struggle with selectivity. This is because these metal-oxides are also sensitive to other reducing gases [48]. However, selectivity can often be improved by modifying the sensor surface with dopants or catalysts, a strategy that has been employed with all these metal-oxides.

Stability, both short-term (over the course of hours or days) and long-term (over the course of months or years), is another important factor in gas sensor performance. Among the metal-oxides discussed here, SnO₂-based sensors have shown good stability, particularly at higher operating temperatures [49]. However, they can suffer from a drift in baseline resistance over time, particularly in fluctuating environmental conditions. In comparison, In₂O₃ and ZnO sensors offer similar levels of stability as SnO₂ sensors. They can maintain their performance over long periods, provided the operating conditions (such as temperature and humidity) are controlled. WO₃ sensors, however, have shown superior long-term stability, even in variable environmental conditions [50]. Their strong performance in this area can be attributed to the robustness of the WO₃ material, which is less susceptible to changes in morphology or loss of active sites over time [51].

Temperature is one of the most significant factors influencing the performance of metal-oxide gas sensors. For SnO₂-based CO sensors, optimal gas sensing usually occurs at elevated temperatures, typically between 200 to 400 °C [52]. The heightened temperature allows for an increased rate of surface reactions, improving the sensor's response towards CO. Similarly, ZnO, In₂O₃, and WO₃-based sensors also exhibit a dependence on temperature. The best response for ZnO and In₂O₃ sensors typically occurs at slightly lower temperatures (150-300 °C) compared to SnO₂ [53]. This characteristic can be an advantage in certain applications where lower operating temperatures are beneficial. WO₃ sensors, however, often require higher operational temperatures (~400 °C) to achieve optimal sensing performance [54]. Therefore, SnO₂-based CO sensors exhibit impressive sensitivity and good stability, but challenges remain in terms of selectivity and performance under variable environmental conditions. Compared to other metal-oxide sensors, such as ZnO, In₂O₃, and WO₃, SnO₂ sensors require relatively high operating temperatures and can be more influenced by humidity and the presence of other gases [55]. However, it is important to note that the limitations of SnO₂ sensors, as well as other metal-oxide sensors, can be mitigated to a certain extent through various strategies. These include the use of nanostructured materials to increase the surface area, doping or loading with catalysts to enhance selectivity and sensitivity, and integration with smart systems for environmental compensation. These strategies, which have been explored in recent advances and will be key to future developments, contribute to the continuously evolving landscape of metal-oxide gas sensors.

Challenges and Limitations

While SnO₂-based CO sensors have shown excellent potential for CO detection, several technical challenges need to be addressed. These challenges stem from

various aspects, including manufacturing, scalability, stability, and environmental factors.

Manufacturing Issues: The manufacturing process of SnO₂-based CO sensors, especially those involving nanostructures, is complex and involves multiple steps, including synthesis, deposition, and annealing. Each step needs careful control to ensure the quality and consistency of the sensors. For example, during the synthesis of SnO₂ nanostructures, parameters, such as the temperature, time, and precursor concentration, need to be precisely controlled to ensure the desired particle size and morphology. In addition, creating uniform and dense nanostructured SnO₂ films on substrates can be challenging. Traditional deposition methods like spin-coating and dip-coating often result in uneven films, leading to inconsistencies in sensor performance. More advanced deposition techniques like atomic layer deposition (ALD) can produce uniform and dense films, but they are costly and time-consuming.

Scalability: Scaling the production of SnO₂-based CO sensors from the lab to industry is another significant challenge. The advanced synthesis methods used to create SnO₂ nanostructures are often not suitable for large-scale production due to their high cost and low throughput. Furthermore, processes such as doping or loading with catalysts, which are crucial for improving sensor performance, can be difficult to scale due to the precise control they require over material composition and microstructure.

Stability: While SnO₂-based CO sensors exhibit good stability in general, they can suffer from performance degradation over time. This can be attributed to various factors, such as changes in the sensor's morphology (e.g., sintering of nanostructures at high operating temperatures), loss of active sites (e.g., desorption of oxygen species), or contamination of the sensor surface. Moreover, the baseline resistance of SnO₂-based CO sensors can drift over time, particularly in fluctuating environmental conditions, leading to false readings. This stability issue poses a significant challenge for the reliable long-term operation of SnO₂-based CO sensors.

Environmental Factors: The performance of SnO₂-based CO sensors is heavily influenced by environmental conditions, such as temperature and humidity. As discussed earlier, these sensors typically require high operating temperatures for optimal performance. This not only increases the energy consumption of the sensors, but also limits their applications in scenarios where high temperatures are not feasible or safe. Humidity is another critical factor influencing the performance of SnO₂-based CO sensors. High levels of humidity can reduce the sensor response due to the competitive adsorption of water molecules on the active sites of SnO₂. This sensitivity to humidity makes SnO₂-based CO sensors less reliable in humid environments or during rainy seasons.

Cross-sensitivity and Selectivity: Another significant technical challenge lies in the cross-sensitivity and selectivity of SnO₂-based CO sensors. Although these sensors are primarily intended for detecting CO, they can respond to other gases present in the environment, leading to inaccurate readings. This is especially problematic in complex environments where multiple gases coexist. For instance, other reducing gases, like hydrogen and methane, can interfere with CO detection, affecting the sensor's selectivity. Recent advancements in catalysts and dopants have improved selectivity to a certain extent; however, it remains a critical area for further research and development.

Future Directions in SnO₂-based CO Sensor Development

Future sensor designs will likely address the challenges mentioned previously, such as stability, selectivity, and scalability. One promising approach is the development of hierarchical and composite structures. Hierarchical structures, which possess features on multiple scales, can enhance gas diffusion and increase the active surface area, thereby improving sensor sensitivity and response speed. Composite structures, where SnO₂ is combined with other materials (like carbon nanotubes, graphene, or other metal oxides), can also offer improved performance. For instance, carbonaceous materials can improve the electrical conductivity of the sensors, while other metal oxides can help in modulating the interaction with gas molecules, thus enhancing selectivity. Moreover, the design of microfabricated and integrated sensor systems is gaining interest. These systems can incorporate multiple sensing elements, signal processing circuitry, and communication modules into a single chip, leading to compact, efficient, and intelligent sensor devices.

In terms of materials, significant advancements are anticipated in the area of nanostructured SnO₂. The ongoing research into various shapes and sizes of SnO₂ nanostructures will undoubtedly continue, with an emphasis on exploring novel structures (like core-shell, hollow, and hybrid structures) that can offer enhanced sensing performance. Further improvements in catalysts and dopants are also expected. While noble metals (like Pd, Pt, Au) and transition metal ions (like Fe, Ni, Co) have been commonly used, other materials (like rare earth elements and organic compounds) are being explored for their potential benefits. In addition, the use of biomolecules or enzymes as catalysts or dopants is an emerging area that could open new possibilities for SnO₂-based CO sensors.

Advancements in manufacturing processes will be critical to overcoming the challenges of scalability and cost. One promising direction is the development of solution-based processes that can produce high-quality SnO₂ nanostructures at a large scale. These

include sol-gel, hydrothermal, and other wet-chemical methods. In addition, techniques such as spray pyrolysis, electrodeposition, and aerosol-jet printing offer potential for depositing nanostructured SnO₂ films in a scalable and cost-effective manner. For high-quality films, ALD and other thin-film deposition techniques are anticipated.

Artificial Intelligence (AI) and Machine Learning (ML) represent a significant leap in enhancing the utility of SnO₂-based CO sensors. The integration of AI and ML can also lead to the development of smart sensor systems. These systems can provide automated data analysis, decision making, and communication capabilities. Shahid et al. [56] constructed a system employs an artificial neural network (ANN) for gas type classification and least squares regression (LSR) for gas concentration estimation (Figure 8). The ANN achieved an impressive 98.7 % accuracy in classifying CO gases based on the unique response patterns of the sensor array. Subsequently, the LSR algorithm was employed to estimate the gas concentrations, yielding high accuracy with minimum values of 94.4 % for CO. This approach demonstrates the viability of real-time and accurate toxic gas detection using the system, which could have significant implications for environmental monitoring and safety measures.

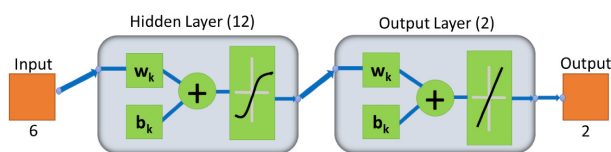


Figure 8. Three-layer ANN for gas classification. Reproduced with permission from Ref. [56].

As SnO₂-based CO sensors evolve, we can expect their deployment to permeate various industry sectors beyond traditional use cases.

Healthcare: In healthcare, these sensors could be instrumental in monitoring the indoor air quality of hospitals and healthcare centres, ensuring patient safety and comfort. Besides, the integration of these sensors into portable medical devices can allow real-time monitoring of CO levels in human breath, which can be a crucial health indicator in conditions like asthma or chronic obstructive pulmonary disease (COPD).

Industrial Automation: The sensors could serve a vital role in the manufacturing industry by monitoring the CO emissions of manufacturing plants and contributing to a safer and more sustainable work environment. Additionally, they can be integrated into various automated systems to control and manage industrial processes more effectively, ensuring product quality and energy efficiency.

Environmental Monitoring: The sensors could be used for large-scale environmental monitoring, including urban air quality monitoring, forest fire detection, and greenhouse gas tracking. Given the miniaturisation trend in sensor technology, we can anticipate the deployment of sensor networks that provide real-time, high-resolution spatial data on CO levels, leading to more effective and timely environmental management and policy-making.

CONCLUSIONS

In conclusion, SnO₂-based CO sensors have emerged as promising candidates for gas detection applications, showcasing notable sensitivity and stability. The recent advancements discussed in this review underscore the potential of these sensors to revolutionise industries ranging from healthcare and environmental monitoring to automotive safety and space exploration. Nanostructured designs, advanced fabrication techniques, and AI integration are key drivers of improved sensor performance. However, challenges, such as manufacturing complexity, scalability, stability, and selectivity, remain, necessitating further research efforts. Future directions in SnO₂-based CO sensor development encompass the pursuit of hierarchical and composite structures, enhanced catalysts, scalable manufacturing methods, and the exploration of diverse applications. The collaborative efforts of researchers, engineers, and industry stakeholders are essential to realising the full potential of SnO₂-based CO sensors and ushering in a new era of safer and smarter sensor technology.

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