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# The Development of Metal Doped Zinc Oxide Nanostructures for Hydrogen Sensors: A Review

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### ABSTRACT

Zinc oxide (ZnO) nanostructures have garnered significant attention as potential materials for hydrogen (H<sub>2</sub>) sensing applications due to their unique properties, such as high surface area, tuneable morphology, and excellent electrical conductivity. The introduction of metal doping into ZnO nanostructures has been shown to enhance their performance by improving sensitivity, selectivity, and response time to H<sub>2</sub> gas. This review provides a comprehensive overview of the advancements in the development of metal-doped ZnO nanostructures for H<sub>2</sub> sensing. Key metal dopants, including transition metals, alkali metals, and rare-earth metals, are discussed in terms of their effects on the structural, electronic, and optical properties of ZnO, which ultimately influence their H<sub>2</sub>-sensing capabilities. The review also examines various techniques employed to fabricate metal-doped ZnO nanostructures, such as sol-gel, hydrothermal, and chemical vapour deposition methods, highlighting their advantages and limitations. Additionally, the mechanisms underlying H<sub>2</sub> sensing in metal-doped ZnO nanostructures, including adsorption, charge transfer, and catalytic effects, are explored. Furthermore, the challenges related to stability, repeatability, and selectivity in real-world applications are addressed. Finally, future research directions and potential strategies for overcoming these challenges, including the exploration of hybrid nanomaterials, composite structures, and the optimisation of doping concentrations, are discussed. This review aims to provide valuable insights for researchers and engineers in the development of advanced H<sub>2</sub> sensors based on metal-doped ZnO nanostructures, contributing to the improvement of safety, energy efficiency, and environmental monitoring.

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## 1. Introduction

Hydrogen ( $H_2$ ) is widely regarded as a promising clean energy carrier due to its high energy density and environmentally friendly combustion byproduct water. Nevertheless, because of its high flammability and broad explosive range,  $H_2$  is essential for industrial and commercial applications in terms of safe handling, storage, and detection [1, 2]. For this reason, creating  $H_2$  sensors that are dependable, sensitive, and selective is crucial to guaranteeing the security of hydrogen-based technology.

Amongst the various materials explored for  $H_2$  sensing, ZnO nanostructures have attracted significant attention due to their unique qualities, such as a high surface-to-volume ratio, superior electrical conductivity, and adjustable optical and electronic characteristics. Furthermore, ZnO has been relied upon as a semiconductor host material considering its advantageous properties, which include a significant exciton binding energy of 60 meV and a direct band gap energy of 3.37 eV [3]. These attributes make ZnO-based sensitive and have faster reaction times. However, pure ZnO has drawbacks such as low selectivity and instability under different environmental conditions. To overcome these issues, metal doping has emerged as a promising technique for improving the  $H_2$  sensing capabilities of ZnO nanostructures [4].

Noble metal and metal doping in  $H_2$  sensors play a crucial role in enhancing the sensitivity, selectivity, and overall performance of the  $H_2$  sensor. Noble metals such as palladium (Pd), platinum (Pt), and gold (Au) are often used due to their excellent catalytic properties and ability to form heterojunctions with metal oxides, which are essential for effective  $H_2$  detection [5-7]. Metal doping, on the other hand, involves incorporating these noble metals into metal oxide matrices to improve the sensor's response to  $H_2$  gas [8,9]. Techniques such as sol-gel synthesis, hydrothermal growth, and chemical vapour deposition have been employed to fabricate these materials, each offering distinct advantages and limitations in terms of scalability, cost, and control over nanostructure morphology [10-12].

Surface interactions influence the  $H_2$ -sensing mechanisms in metal-doped ZnO nanostructures, which include  $H_2$  adsorption, charge transfer processes, and catalytic effects. These processes are regulated by the type of metal, concentration, and distribution of dopants inside the ZnO lattice, as well as the sensor's operating parameters [13, 14]. Despite tremendous advances, issues with long-term stability, reproducibility, and selectivity in real-world applications remain. To address these issues, creative techniques are required, such as the creation of hybrid nanomaterials, nanostructures, and enhanced doping techniques.

Therefore, this study aims to address the performance constraints of pure ZnO by studying noble metal-doped ZnO nanostructures. It aims to improve the sensitivity, selectivity, and durability of hydrogen sensors by using optimum doping strategies and synthesis procedures, subsequently leading to the development of safer and more efficient hydrogen detection devices for clean energy technologies.

## 2. Hydrogen Sensor Mechanism

### 2.1 Heated Hydrogen Sensor

Most semiconductor  $H_2$  sensors have weak response, slow-paced response, and delayed recovery at room temperature. Therefore, to improve the reaction rate, semiconductor-based gas sensors often require heating to a very high temperature. There are several ways to categorise the reaction process. First, oxygen molecules will absorb electrons from the semiconductor surface when the detecting layer is exposed to air. They will then separate to create multiple forms, including

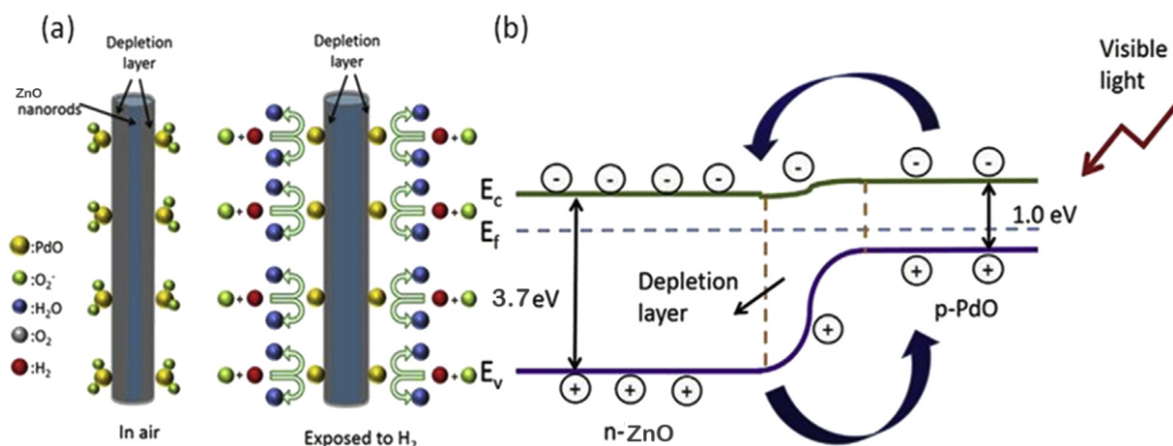
single-ionised ( $O^-$ ), ionised molecules ( $O^{2-}$ ), and double-ionised oxygen ions ( $O_2^-$ ). This adsorbed oxygen takes electrons from the conduction band of ZnO NWs and forms ionic oxygen species, which, depending on the temperature, may cause an increase in electrical resistance [15]. The following possible reactions may occur at the interface.



Since  $H_2$  is a reducing gas, its affinity is less than the semiconductor surface's work function. As a result, gas molecules' electrons will be moved to semiconductor surfaces to create  $H^+$  ions. This will lower the resistance and raise the surface electron concentration in n-type semiconductors, ZnO. It will raise the resistance and lower the concentration of holes in p-type semiconductors [16-18].  $H^+$  ions will combine with those oxygen species to produce  $H_2O$  on the surface when those sensors in the air are transferred into  $H_2$ . The resistance changes when the kind of semiconductor changes because those electrons that were desorbed during the reaction process will go into the adsorbed oxygen and subsequently be liberated into semiconductors [19, 20]. Measuring the change in resistance makes it simple to determine the sensor sensitivity. According to Liu [20], metal-oxide semiconductors' sensing capabilities are significantly impacted by their grain size. The conductivity of sensors is primarily influenced by the concentration of carriers within the grain, meaning that surface reactions have minimal effect on the resistance of the grain if the grain size ( $D$ ) is significantly larger than  $2L$  (where  $L$  is the thickness of the electron depletion layer). In this instance, the sensors' sensitivity to the target gas is minimal. Grain borders have little influence on internal charge transfer if  $D$  is less than  $2L$ , the depletion layer covers the whole grain, and the energy bands inside the grain are almost identical. The depletion layer primarily determines conductivity; even a slight variation in charges can significantly affect sensor resistance [22, 23].

## 2.2 Room Temperature Hydrogen Sensor

It is more difficult to excite electrons in a room temperature  $H_2$  sensor since its working temperature is significantly lower than that of a heated  $H_2$  sensor. Finding an alternative technique to efficiently separate the electron-hole pairs is essential to increasing its sensitivity at room temperature. In addition to the dissociation of oxygen and the interaction between  $H_2$  and adsorbed oxygen, electron-hole pairs will also be stimulated and separated at depletion layers close to the surface when additional techniques, including visible light irradiation, are used. As seen in Figure 1, the holes will then react with those adsorbed oxygen at the interfaces and thin the depletion layers, consuming the holes and altering the semiconductor's resistance [23]. ZnO semiconductors have broad band gaps, meaning they are difficult to excite since their band gaps are wider than 3.0 eV.



**Fig. 1.** Schematic of (a) the carrier excited process in the PdO-ZnO nanohybrids under visible light illumination, and (b) the sensing process of PdO-ZnO nanohybrids exposed to air and H<sub>2</sub> gas, respectively

### 3. Mechanism of Sensitivity Enhancement with Metal Doping

Metal doping decoration improves sensitivity in ZnO H<sub>2</sub> sensors because of the metal clusters' catalytic properties, which allow hydrogen molecules to adsorb and react on the sensor surface. This process involves various mechanisms, including the spill-over effect, electron transfer, and the development of active sites, which increase the sensor's response to H<sub>2</sub> gas [24, 25]. The incorporation of metal doping including palladium (Pd), platinum (Pt), and gold (Au) with ZnO nanostructures significantly improves the sensor's performance by boosting sensitivity, selectivity, and stability.

Noble metals like Pd, Pt, and Au can act as catalysts, enhancing the dissociation of hydrogen molecules through the spill-over effect. The spillover effect happens when a gas adsorbs on one phase (in this example, the metal cluster) and subsequently dissociates. The dissociated species go to the second phase (the supporting semiconductor) and get activated. Adsorption of these activated species in the second phase was observed, which could not have happened under the same conditions [26]. In the case of gas sensing, this means that molecules from the target gas first react with noble metals in the sensing layer, resulting in active species. Then, these species are adsorbed onto the surface of metal oxide, affecting its sensing capabilities. Consider Pd, which can separate H from H<sub>2</sub>. After that, H spills over and becomes adsorbed on the surface of ZnO. The job of Pd is to reduce the reaction activation energy. This reduces reaction and recovery times while also lowering operational temperatures [27].

Furthermore, because the Fermi levels of doping metals are frequently lower than those of semiconductors used for gas sensing, charge carriers are redistributed, and electrons are transferred from the semiconductor to the metal until the Fermi levels of the two materials meet. During this process, metals become negatively charged and semiconductors become positively charged. At the interfaces, the semiconductor's energy bands twist, generating a Schottky barrier. The Schottky barrier may effectively restrict the recombination of separated electron-hole pairs, hence enhancing responsiveness to the target gas [28], [29]. Another scenario occurs when noble metal atoms enter the semiconductor lattice and replace certain metal atoms. When this process occurs, the enhanced mechanism will experience some changes. Using ZnO as an example, substituting some of the Zn<sup>2+</sup> in the lattice with noble metals alters the lattice parameter and bond length. As a result, the octahedron's positive and negative charge centres will shift, creating dipole moments inside. Then, a local electric field will be generated across the crystal, allowing electron-hole pair separation.

The presence of metal clusters on ZnO surfaces leads to enhanced electron transfer processes by providing additional pathways for electron transport, thereby increasing the number of charge carriers and improving sensor conductivity. This effect is particularly evident in Pd-decorated ZnO, where the electron back-donation mechanism plays a crucial role in modulating the sensor's resistivity [30]. Furthermore, the formation of metal-oxide interfaces creates Schottky barriers, which modulate the flow of charge carriers and improve the sensor's response to H<sub>2</sub> gas [31].

Metal clusters also modify the surface properties of ZnO, creating new active sites that enhance the adsorption and reaction of hydrogen molecules. The decoration of ZnO with noble metals increases the surface area and the number of reactive sites available for gas interaction [31, 32]. The use of bimetallic clusters, such as Au-Pt, further enhances sensor performance by providing a synergistic effect that improves both sensitivity and selectivity for H<sub>2</sub> detection [32].

#### **4. Metal-doped ZnO Hydrogen Sensor**

##### **4.1 Al-Doped ZnO Hydrogen Sensor**

The electronic transport properties of ZnO are primarily influenced by non-stoichiometric defects, such as oxygen vacancies, and impurities like dopants, which determine its conductivity type [33]. Group III impurities, such as aluminium (Al), typically induce n-type conductivity in ZnO [34]. As a metal dopant, Al plays a crucial role in enhancing the performance of ZnO-based gas sensors. One method is that the incorporation of Al into ZnO structures improves electrical conductivity due to the smaller ionic radius of Al<sup>3+</sup> (0.054 nm) compared to Zn<sup>2+</sup> (0.074 nm), leading to increased carrier concentration and enhanced sensor efficiency [35]. Aluminum-doped ZnO (AZO) sensors can increase the sensitivity and selectivity of H<sub>2</sub> sensors. The addition of aluminium to ZnO nanostructures changes the electrical and surface characteristics, which are important for gas sensing applications. For example, Hosseinnjad et al. investigated the deposition, and H<sub>2</sub> gas sensing capability of AZO thin films manufactured with a low-energy plasma focus (PF) device [36]. The films were formed on glass substrates at various angles (0°, 10°, and 25°) relative to the anode axis. While the gas sensing studies at 300°C and 1000 ppm H<sub>2</sub> concentration revealed that the film deposited at 25° had the highest response (69%) and quickest reaction time, owing to improved surface contacts and increased defect sites.

In separate studies, Chatterjee et al. investigated the H<sub>2</sub> gas sensing capabilities of AZO metasurfaces, with an emphasis on nanotube architectures with optical readout [37]. The researchers created AZO nanotubes and solid AZO pillars with sophisticated nanofabrication techniques such as atomic layer deposition (ALD) and deep-UV lithography. Optical gas sensing investigations with a high-resolution spectroscopic ellipsometer indicated that AZO nanotubes showed a considerable wavelength shift and drop in reflectance intensity when exposed to H<sub>2</sub>, even at low concentrations (0.7%). In contrast, solid AZO pillars did not respond. Finite Element Method (FEM) simulations revealed a 17 nm wavelength shift and increased electromagnetic field interactions in the nanotubes, which explains their high sensitivity.

Another technique is ultrasonic spray pyrolysis by Eensalu et al. have success produced H<sub>2</sub> gas sensor of AZO thin films [38]. The films were deposited on soda lime glass at various temperatures (280-400 °C) and aluminum concentrations (2-30 % AZO). Their gas sensing studies tested the films' resistance to H<sub>2</sub> (3%) at temperatures ranging from 60 to 100°C. The maximum sensor response (11%) was reported at 100 °C for AZO-5 films formed at 280 °C. Films deposited at 400 °C had lower responses but better stability and faster recovery. Higher Al doping levels (≥10 at%) resulted in worse sensing performance due to higher film resistance. Overall, AZO-2 and AZO-5 films demonstrated

good H<sub>2</sub> detecting capabilities, with quick response (3-6 s) and recovery (5-11 s), making them ideal for low-temperature sensor applications.

Another Innovative approach by Lin et al. investigated a H<sub>2</sub> sensor that combined an AZO layer with Pd nanoparticles to improve sensing capability [39]. The AZO layer was sputtered onto a sapphire substrate with Cr/Pt interdigitated electrodes (IDEs), followed by the deposition of Pd NPs via vapor transport epitaxy. After manufacturing, the gadget was annealed to stabilize the materials. Gas sensing investigations indicated a chemiresistive response, indicating that resistance reduced with H<sub>2</sub> exposure. The sensor had a high sensing response ( $1.86 \times 10^4$  at 1% H<sub>2</sub>/air and 250°C) and ideal working temperature of 250°C. It had a low detection limit (50 ppb H<sub>2</sub>/air) and remained stable for 90 days.

To investigate the increase of H<sub>2</sub> gas sensing characteristics of AZO films. Al-Hardan et al. use the thermal oxidation to fabricate the AZO H<sub>2</sub> sensor [40]. The experimental procedure involves producing Zn and AZO thin films onto silicon substrates using DC sputtering, followed by oxidation in a controlled tube furnace at 400°C. Characterization validated the conversion of Zn to ZnO and revealed polycrystalline structures with changed peak intensities because of Al doping. Electrical experiments revealed that AZO had lower resistance than undoped ZnO, which was attributable to enhanced charge carrier concentration. The gas detecting ability was examined by subjecting the sensors to varied H<sub>2</sub> gas concentrations (0-120 ppm), revealing a considerable improvement in responsiveness, particularly at low working temperatures. As the temperature dropped from 400°C to 300°C, the sensing response of AZO rose from around 100 to 2000, indicating better sensitivity. Furthermore, Al doping resulted in larger output current and reduced baseline resistance, which improved surface activity and gas interaction. The AZO sensor showed faster responsiveness and a lower operating temperature than undoped ZnO, making it an attractive choice for low-level H<sub>2</sub> detection applications. Table 1 shows the parameters of sensors mentioned before.

**Table 1**  
Hydrogen sensing properties of Aluminium-doped ZnO sensors

| Structure   | Definition of Sensitivity                                 | Concentration | Operating Temperature | Sensitivity | Response time | Ref  |
|-------------|-----------------------------------------------------------|---------------|-----------------------|-------------|---------------|------|
| Thick films | $S = \left[ \frac{(R_a - R_g)}{R_a} \right] \times 100\%$ | 1000 ppm      | 300 °C                | 69 %        | 198 s         | [36] |
| Nanotubes   | $S = \frac{R (AZO_{air})}{R (AZO_{H2})} \times 100$       | 0.7 %         | Room Temperature      | 104         | 10 mins       | [37] |
| Leaf-like   | $S = \frac{R_{gas} - R_{air}}{R_{air}} \times 100\%$      | 3 %           | 60 °C                 | 8 %         | 3 s           | [38] |
| Nano device | $S_R = \frac{R_{air} - R_{H2}}{R_{H2}}$                   | 0.05 ppm      | 250 °C                | 1 %         | 25 s          | [39] |
| Thin films  | $S = \frac{R_a}{R_g}$                                     | 120 ppm       | 300 °C                | 2100        | -             | [40] |

#### 4.2 Mg-Doped ZnO Hydrogen Sensor

Mg-doped ZnO (MgZO) is one of the most extensively studied doped ZnO materials, offering advantages such as a tenable bandgap, minimal lattice mismatch with ZnO, and high crystal quality with fewer oxygen vacancies. The incorporation of Mg<sup>2+</sup> into the ZnO matrix alters the grain shape and size, enhancing its structural properties. The high reactivity efficiency of MgZO films toward H<sub>2</sub> is attributed to the increased surface activity of smaller ZnO particles on the substrate. Improved sensing performance results from a reduced residual electron concentration due to Mg substitution

and the chemical sensitization effect of Mg atoms [42, 43]. Several studies have explored the application of MgZO in gas sensors.

Firstly, Lin et al. explore the H<sub>2</sub> sensing characteristics of MgZO thin films produced via RF co-sputtering [43]. The experiment entailed depositing MgZO films of different thicknesses (132-836 nm) on silicon substrates. The study demonstrated that film thickness greatly influenced H<sub>2</sub> sensing, with a 423 nm film obtaining the best sensitivity (2.46) at 300°C when exposed to 1000 ppm of H<sub>2</sub>. The sensing method was linked to resistance variations caused by H<sub>2</sub>-induced electron donation and oxygen vacancy creation. Temperature also had an important impact, since sensitivity rose with operational temperature and peaked at 300°C. Thicker films exhibited enhanced defect formation, improving sensitivity, but excessive thickness led to reduced gas interaction and slower response/recovery times.

Another notable study by Liu et al. compares the H<sub>2</sub> sensing performance of MgZO thin films to undoped ZnO films made with pulsed laser deposition (PLD) [44]. The experimental results showed that MgZO films had much higher H<sub>2</sub> sensitivity. X-ray diffraction demonstrated that 10% Mg doping did not change the ZnO crystal structure, whereas atomic force microscopy revealed that the MgZO film had a considerably smoother surface than undoped ZnO. Gas sensing studies revealed that MgZO films responded adequately to hydrogen concentrations as low as 5 ppm, but ZnO needed at least 200 ppm for detectable levels. At 300°C, the MgZO sensor responded 15 at 5 ppm H<sub>2</sub> and 50 at 5000 ppm, but the undoped ZnO sensor only reached 2.9 at 5000 ppm. MgZO's higher performance was due to its lower initial conductivity, which results in a more noticeable shift in resistance following H<sub>2</sub> exposure.

Similarly, Karthick et al. studied the production and performance of MgZO thin films as H<sub>2</sub> gas sensors, focusing on their potential for room-temperature operation [45]. The researchers used RF magnetron sputtering to create MgZO films on Al<sub>2</sub>O<sub>3</sub> substrates. They systematically varied substrate temperatures to analyse the impacts on structural, optical, and gas-sensing capabilities. Photoluminescence investigation demonstrated a shift in emission peaks owing to changes in crystallite size and defect elimination, whilst optical experiments revealed a modest decrease in the band gap at higher temperatures. Morphological investigation revealed that films formed at 1400 °C had denser, bigger nanorods with increased roughness, which improved gas-sensing performance. The H<sub>2</sub> sensing studies showed a quick and consistent response, with resistance reducing with H<sub>2</sub> exposure due to electron release from adsorbed oxygen species. The sensor constructed at 1400 °C displayed enhanced response and recovery durations (75s and 54s, respectively), indicating its usefulness in detecting H<sub>2</sub> at ambient temperature.

On the other hand, Bangale et al. investigated the construction of a H<sub>2</sub> sensor employing nanostructured MgZO manufactured by self-combustion [46]. Screen-printing was used to create thick MgZO sheets, which were then annealed at high temperatures. The electrical and gas sensing capabilities of the films were studied, indicating a high sensitivity to H<sub>2</sub> gas at an ideal temperature of 200 °C. The sensor responded quickly, in around 10 seconds, and recovered in 20 seconds, with a maximum gas response of 1.35 for 100 ppm H<sub>2</sub>. According to the selectivity analysis, MgZO was the most sensitive to H<sub>2</sub> when compared to other gases such as chlorine, ammonia, LPG, and acetone. The sensing mechanism was linked to the adsorption-desorption process of oxygen species on the sensor surface, which influenced conductivity variations when exposed to H<sub>2</sub>.

Lastly, Vijayalakshmi et al. studied how Mg doping affects the morphology, optical characteristics, and H<sub>2</sub> sensing capabilities of ZnO thin films [47]. ZnO and MgZO films were produced on C-cut sapphire substrates using direct current magnetron. The findings revealed that Mg doping increased the crystallinity of ZnO films while preserving their hexagonal wurtzite structure. The doped films had a bandgap shift of 3.25 eV to 3.54 eV, indicating increased optical transparency and

altered electronic characteristics. At lower operating temperatures, 180°C, MgZnO performed better than pure ZnO, exhibiting enhanced adsorption sites, shorter response times, and superior sensitivity because of its larger surface area and lattice. Analysis of the surface morphology showed that MgZnO exhibited more nanostructures, higher surface roughness, and smaller grain sizes, all of which enhanced gas sensing capability. Table 2 shows the parameters of sensors mentioned before.

**Table 2**  
Hydrogen sensing properties of Magnesium-doped ZnO sensors

| Structures       | Definition of Sensitivity   | Concentration | Operating Temperature | Sensitivity | Response time | Ref  |
|------------------|-----------------------------|---------------|-----------------------|-------------|---------------|------|
| Thick films      | $S = \frac{R_a}{R_g}$       | 1000 ppm      | 300°C                 | 2.46        | 280 s         | [43] |
| Thin films       | $S = \frac{R_a}{R_g}$       | 5000 ppm      | 300°C                 | 50          | 10 min        | [44] |
| Thin films       | -                           | 200 ppm       | 1400°C                | -           | 75 s          | [45] |
| Thick films      | $S = \frac{G_g + G_a}{G_a}$ | 100 ppm       | 200°C                 | 1.35        | 10 s          | [46] |
| Micro-structures | $S = \frac{R_a}{R_g}$       | 200 ppm       | 180°C                 | 95          | -             | [47] |

#### 4.3 Mn-Doped ZnO Hydrogen Sensor

The doping of ZnO with transition metals, such as manganese ion ( $Mn^{2+}$ ), has proven to be highly beneficial in enhancing gas sensor performance. Manganese ions act as donor impurities, and their integration into the ZnO crystal structure increases the concentration of free electrons, thereby improving conductivity. In a study by Allawai et al., manganese-doped ZnO (MnZO) thin films were synthesized and characterized for  $H_2$  gas sensing using spray pyrolysis at 400°C [48]. The research examined the effects of Mn doping on the structural, optical, and electrical properties of ZnO films. The MnZO films exhibited spherical nano-grains, with grain size increasing from 12.66 nm to 14.66 nm at 3% Mn doping, which enhanced crystallinity. Optical transmittance measurements showed a decrease in transmittance and an increase in absorption coefficients with higher Mn content, indicating alterations in the electronic structure. Additionally, the bandgap of the films was reduced by Mn doping, affecting their optical properties. Gas sensing tests revealed that Mn-doped ZnO exhibited higher resistance upon  $H_2$  exposure, with the optimal sensitivity observed at a 3% Mn concentration.

In a different approach, Renitta et al. focused on utilizing MnZO nanowire arrays for  $H_2$  gas sensing. These nanowires were grown on an ITO-coated glass substrate via chemical spray pyrolysis [49]. Mn doping influenced lattice distortion, strain, and crystallite size, while a decrease in transmittance and bandgap was observed with increasing Mn concentration, which was attributed to enhanced defect states and charge carrier interactions. With increasing Mn concentration causing variations in grain size and morphology, thus enhancing the number of gas adsorption sites. The gas sensing performance of Mn-doped ZnO nanowires demonstrated high sensitivity, rapid response, and stability at room temperature, with the best response observed at 4% Mn doping.

Meanwhile, Kovalenko et al. conducted a study on the impact of hydrogen heat treatment on the gas sensitivity of MnZO nanocrystals. These nanocrystals were synthesized via ultrasonic aerosol pyrolysis [50]. The MnZO nanocrystals underwent thermal treatment at 550°C in a hydrogen atmosphere, which led to significant structural and electronic modifications. Electron paramagnetic resonance (EPR) spectroscopy revealed an increase in defect concentration, especially oxygen vacancies, which are crucial for gas adsorption. The sensors, made by compacting the nanocrystals

into pill forms at an optimized pressure of 140 MPa, demonstrated enhanced sensitivity to H<sub>2</sub> gas due to the formation of donor complexes and enhanced charge carrier concentration. The study concluded that hydrogen modification effectively enhances the gas sensitivity of MnZO nanocrystals, enabling lower operating temperatures and faster response times.

Additionally, Anjali et al. explored the potential of manganese doping to enhance ZnO thin-film H<sub>2</sub> gas sensors. Their aim was to increase sensitivity while reducing the operating temperature [51]. Using semiconductor metal oxide properties and nanotechnology, the researchers fabricated the sensors by depositing manganese-doped ZnO nanoparticles onto a glass substrate using chemical deposition methods. The sensor's operation relies on receptor-transducer interactions, where gas adsorption alters electrical resistance through electron exchange with oxygen species on the ZnO surface. Experimental tests using a controlled chamber setup with high-purity H<sub>2</sub> gas and resistance measurements demonstrated that manganese doping reduced the sensor's optimal operating temperature from 200°C to 190°C, while maintaining high sensitivity. These findings highlight the benefits of manganese incorporation, which enhances chemical interactions, lowers surface resistance, and enhances response time, making it a promising strategy for efficient H<sub>2</sub> detection.

Lastly, Priyanka et al. investigated the synthesis and characterization of MnZO nanoparticles for H<sub>2</sub> gas sensing. Their research focused on understanding the impact of Mn doping on the structural, optical, and gas-sensing properties of ZnO [52]. Structural analysis confirmed a wurtzite crystalline phase, with Mn doping causing lattice expansion or contraction depending on the oxidation state. SEM images revealed a morphological transformation from nanorods to flower-like structures with increased Mn content. Optical studies indicated a shift in the bandgap due to Mn doping, while photoluminescence spectra showed reduced emission intensity because of an increase in non-radiative recombination centers. Gas sensing tests demonstrated enhanced hydrogen sensitivity at 250°C, particularly for ZnO doped with 4% Mn (x = 0.04), which exhibited the highest response due to smaller particle size, increased oxygen vacancies, and greater surface reactivity. Table 3 shows the parameters of sensors mentioned before.

**Table 3**  
Hydrogen sensing properties of Manganese-doped ZnO sensors

| Structure | Definition of Sensitivity                               | Concentration | Operating Temperature | Sensitivity | Response time | Ref  |
|-----------|---------------------------------------------------------|---------------|-----------------------|-------------|---------------|------|
| Cubic     | $S = \left  \frac{R_g - R_a}{R_g} \right  \times 100\%$ | 180 ppm       | 400 °C                | 53.6 %      | 80 s          | [48] |
| Nanowires | $S = \frac{R_a}{R_g}$                                   | 200 ppm       | RT                    | 122         | -             | [49] |
| Nanorods  | $S = \frac{R_a - R_g}{R_a}$                             | 10 %          | 95 °C                 | 0.44        | 200 s         | [50] |
| Thin film | $S = \frac{R_a}{R_g}$                                   | 100 000 ppm   | 200°C                 | 15          | 20 min        | [51] |
| Nanorods  | $S = \frac{R_a - R_g}{R_a} \times 100\%$                | 10 000 ppm    | 250°C                 | 54.24 %     | -             | [52] |

### 3.4 Co-Doped ZnO Hydrogen Sensor

Cobalt-doped ZnO (CZO) gas sensors have emerged as a promising solution for efficient H<sub>2</sub> detection due to their enhanced sensitivity, selectivity, and stability. By incorporating cobalt into the ZnO structure, significant improvement in gas adsorption, conductivity, and response-recovery characteristics can be achieved. The study by Dmello et al. explores the development of a room-

temperature chemiresistive  $H_2$  sensor using CZO nanostructures anchored on nitrogen-doped carbon, synthesized via a metal-organic framework (MOF) technique [53]. The technique involves pyrolysis of Zeolite Imidazole Frameworks (ZIFs) under nitrogen flow to produce ZnO nanostructures with high dispersion and porosity. Gas sensing performance tests reveal that CZO exhibits a significantly higher response, rapid response-recovery times, and enhanced selectivity for  $H_2$  at room temperature compared to undoped ZnO. The study highlights that Co doping enhances ZnO conductivity and gas adsorption capabilities, optimizing the material's performance under a 5 V bias. Compared to other ZnO-based sensors, CZO demonstrates superior  $H_2$  sensing due to its unique nanostructure and noble metal-free composition.

Another promising approach to improving  $H_2$  sensing involves the use of CZO nanofibers. The study by Lee et al. investigates the development of CZO nanofiber-based  $H_2$  sensors, synthesized using an electrospinning technique to enhance gas-sensing performance [54]. The composite nanofibers demonstrated superior  $H_2$  response at  $300^\circ\text{C}$  compared to pristine ZnO nanofibers. Gas-sensing tests revealed a significant reduction in resistance upon  $H_2$  exposure, attributed to increased free-electron concentration in ZnO and surface metallization effects. The sensor exhibited high selectivity for  $H_2$  over carbon oxide and nitrogen dioxide, with a low detection limit around 5.34 ppb and rapid response-recovery times at 70s.

A different synthesis method, the sol-gel technique, was employed by Moosavi et al. to investigate the  $H_2$  sensing properties of CZO nanoparticles [55]. The study focused on optimizing the sensitivity and selectivity of ZnO-based conductometric sensors for detecting low  $H_2$  concentrations at moderate temperatures. The gas sensor was fabricated by depositing the synthesized nanoparticles onto  $Al_2O_3$  substrates with interdigitated Pt electrodes and a resistive heater. Gas sensing experiments revealed that Co-doping led to a transition from n-type to p-type behaviour, reducing the response to  $H_2$  but significantly improving selectivity against volatile organic compounds (VOCs) such as ethanol and acetone. The enhanced selectivity was attributed to changes in oxygen vacancies, acid-base characteristics, and the formation of CZO. The optimal sensing temperature for  $H_2$  detection was determined to be  $150^\circ\text{C}$ , with the sensor exhibiting a fast response and recovery time, minimal hysteresis, and a detection limit of approximately 1 ppm.

The hydrothermal synthesis method was explored by Sett et al. to enhance  $H_2$  gas sensing using CZO nanorods [56]. The study found that Co doping, particularly at 8 mol, significantly enhanced the  $H_2$  gas response, with a fivefold improvement compared to undoped ZnO nanorods at  $150^\circ\text{C}$ . The optimal Co doping level led to faster response times, 80s, and higher sensitivity to  $H_2$ , with a gas response of 53.7% at 3000 ppm, compared to just 11% for undoped ZnO. The mechanism behind this enhancement is attributed to the introduction of donor-related oxygen vacancies ( $V_o$ ) by Co dopants, which increase surface defect sites, thereby improving adsorption behaviour and conductivity.

Ghosh et al. investigated the  $H_2$  sensing properties of CZO thin films, particularly focusing on the conductivity reversal phenomenon and its selective response to  $H_2$  [57]. The study found that cobalt doping, particularly at 0.01 %, induced a reversal of conductivity from n-type to p-type when exposed to  $H_2$  gas at  $200^\circ\text{C}$ . The CZO thin films exhibited a high response of 220.6 % at  $200^\circ\text{C}$ , enabling selective detection of  $H_2$  compared to other gases, which maintained n-type conductivity at higher temperatures. The sensing mechanism involved the formation of hydroxide ion at lower temperatures, which increased resistance, while higher temperatures led to increased conductivity through oxygen vacancy desorption. Langmuir adsorption kinetics were used to model the conductance transient, providing insights into the response and recovery times. Additionally, principal component analysis (PCA) revealed that at  $200^\circ\text{C}$ , the sensor distinctly identified  $H_2$  from other gasses, addressing cross-sensitivity issues. Table 4 shows the parameters of sensors mentioned before.

**Table 4**  
**Hydrogen sensing properties of Cobalt-doped ZnO sensors**

| Structure          | Definition of Sensitivity                             | Concentration | Operating Temperature | Sensitivity | Response time | Ref  |
|--------------------|-------------------------------------------------------|---------------|-----------------------|-------------|---------------|------|
| Rhombohedron shape | -                                                     | 1 %           | 200 °C                | 5.9 %       | 8 s           | [53] |
| Nanofibers         | $S = \frac{R_a}{R_g}$                                 | 10 ppm        | 300 °C                | 133         | 70 s          | [54] |
| Nanoparticles      | $S = \frac{R_g}{R_a}$                                 | 50 ppm        | 200 °C                | 18          | 20 s          | [55] |
| Nanorods           | $S = \left  \frac{I_g - I_a}{I_a} \right  \times 100$ | 300 ppm       | 150 °C                | 53.7 %      | 74 s          | [56] |
| Thin film          | $S = \alpha C^{0.69}$                                 | 500 ppm       | 200 °C                | 220.6 %     | -             | [57] |

## 5. Noble Metal-doped ZnO Hydrogen Sensor

### 5.1 Pd-Doped ZnO Hydrogen Sensor

Palladium (Pd) is one of the most effective catalytic materials for H<sub>2</sub> sensing due to its strong chemisorption properties at room temperature [5]. The sensing mechanism involves the dissociation of H<sub>2</sub> molecules into H<sub>2</sub> atoms, forming PdH<sub>x</sub>, which can lead to significant volume expansion[58]. However, Pd is prone to delamination during sensing operations, making ZnO a suitable n-type semiconductor shell to enhance stability, sensitivity, and response time while protecting the Pd surface [59].

One approach to improving H<sub>2</sub> sensing in oxygen-free environments involves the use of Pd-doped ZnO (PdZO) nanofibers. Platonov et al. investigated the H<sub>2</sub> sensing properties of electrospun PdZO nanofibers in an oxygen-free environment[60]. ZnO and PdZO nanofibers were produced by electrospinning, then annealed at 550°C. Gas sensing studies demonstrated that, while the sensor response to carbon monoxide remained consistent across different oxygen concentrations, the response to H<sub>2</sub> and ammonia rose dramatically in oxygen-deficient condition. This H<sub>2</sub> absorption process resulted in significant electron transfer and resistance changes, which enhanced the sensor's efficacy in detecting H<sub>2</sub> at ultralow oxygen levels. The work focuses on PdZO nanofibers as very sensitive materials for H<sub>2</sub> detection in oxygen-free settings.

A different strategy to enhance H<sub>2</sub> sensing performance is through Pd decoration of ultrathin ZnO nanosheets. Kim et al. analyse the H<sub>2</sub> sensing characteristics of ultrathin ZnO nanosheets coated with Pd that were manufactured using a solvothermal process and then modified using UV irradiation [61]. ZnO nanosheets having a thickness of around 1 nm were dip-coated onto quartz substrates. Pd decorating was obtained by immersing them in a PdCl<sub>2</sub> solution, followed by UV irradiation and annealing. Gas sensing studies showed that Pd decorating considerably enhanced H<sub>2</sub> detection, lowering the ideal operating temperature to 250°C and increasing selectivity by eliminating interference from other gases. The sensor's response mechanism is linked to Pd's catalytic activity, which facilitated H<sub>2</sub> dissociation and electron transfer, resulting in a resistance decrease when exposed to H<sub>2</sub>. Furthermore, PdH<sub>x</sub> manufacturing enhanced sensitivity, while the lower self-heating voltage suggested less power consumption. The flexible sensors performed consistently under mechanical stress, indicating their suitability for real-world applications. Overall, Pd decoration enhanced the sensor's H<sub>2</sub> response, lowered power requirements, and increased selectivity, making it a promising technology for efficient H<sub>2</sub> detection in safety and energy applications.

Another approach involves integrating PdZO nanostructures with optical fibre technology. Yahya et al. demonstrate a H<sub>2</sub> gas sensor based on PdZO nanostructures deposited on a tapered

optical fiber [62]. The ZnO nanostructures were created using a chemical bath deposition (CBD) process and applied to a tapered multimode silica optical fibre. The deposition period was adjusted to regulate the thickness of the ZnO layer, which was determined to be best at 280 nm. The sensor was tested at 180°C with varying H<sub>2</sub> concentrations in synthetic air and demonstrated a considerable absorbance response, notably in the 700-1000 nm wavelength region. The annealing procedure increased the crystallinity of ZnO and produced oxygen vacancies, which enhanced the sensor's gas chromic characteristics. When exposed to 1% H<sub>2</sub>, the annealed PdZO sensor with a thickness of 280 nm showed a 64% improvement in absorbance response compared to the as-prepared equivalent. The study also found that smaller ZnO layers resulted in faster reaction and recovery periods, but bigger layers delayed these times.

Further research paper by Yahya et al. created a highly selective H<sub>2</sub> gas sensor using a PdZO-coated tapered optical fibre [63]. The experiment involves creating ZnO nanostructures by chemical bath deposition, then annealing and palladium plating. The sensor's absorbance response was evaluated at 180°C with H<sub>2</sub>, methene, and ammonia gases, revealing greater selectivity for H<sub>2</sub> (86.8%) over methane (8.4%) and ammonia (4.7%). The Pd catalyst significantly reduced the sensor's operating temperature while increasing sensitivity.

For applications requiring flexibility and selectivity at ambient temperature, self-assembled membrane coatings offer a promising solution. Pathak et al. investigated a PdZO flexible H<sub>2</sub> sensor with a self-assembled 1-octadecanethiol membrane to increase selectivity at ambient temperature [64]. The manufacturing procedure included screen printing a ZnO nanoparticle paste onto a flexible polyimide substrate, followed by sputter deposition of a Pd thin layer and subsequent annealing to stimulate Pd nanoparticle production. The gas sensing characterisation revealed a steady, quick reaction to H<sub>2</sub>, with response times dropping from 68s to 43s as H<sub>2</sub> concentrations grew from 0.1% to 2%. The hydrophobic nature and low water vapor permeability of the 1-octadecanethiol membrane resulted in the sensor's great selectivity, with negligible reaction to interfering gases such as methane, ethanol, acetone, and wet air. Table 5 shows the parameters of sensors mentioned before.

**Table 5**  
Hydrogen sensing properties of Palladium-doped ZnO sensors

| Structure     | Definition of Sensitivity | Concentration | Operating Temperature | Sensitivity | Response time | Ref  |
|---------------|---------------------------|---------------|-----------------------|-------------|---------------|------|
| Nanofibers    | $S = \frac{R_0}{R} - 1$   | 35 ppm        | 100°C                 | 0.0005%     | -             | [60] |
| Nanosheets    | $S = \frac{R_a}{R_g}$     | 50 ppm        | 25 °C                 | 2.514       | -             | [61] |
| Thick films   | -                         | 1 %           | 180 °C                | 1.921       | 3 min         | [62] |
| Nanoflowers   | -                         | 1 %           | 180 °C                | 86.6%       | -             | [63] |
| Nanoparticles | $S = \frac{R_a}{R_g}$     | 2 %           | RT                    | 186         | 43 s          | [64] |

## 5.2 Ag-Doped ZnO Hydrogen Sensor

Ag nanoparticles capable of serving as catalysts by accelerating the chemisorption of ambient oxygen, creating additional adsorption sites on the metal oxide surface and significantly enhancing gas-sensing performance [65]. As an alternative metal, Ag offers high solubility, a larger ionic size, and minimal orbital energy, making it an excellent additive for ZnO-based sensors. Ag-doped ZnO (AgZO) lowers processing temperatures, enhances light absorption, and alters structural, optical, and

electrical properties. Additionally, Ag enhances luminescence, chemical reactivity, and electron transfer while modifying the material's surface structure and increasing its surface area [67, 68].

One of the promising advancements in H<sub>2</sub> gas sensing involves the development of AgZO-In<sub>2</sub>O<sub>3</sub> nanocomposites. The study by Yuan et al. focuses on developing AgZO-In<sub>2</sub>O<sub>3</sub> nanocomposites for low-temperature rapid H<sub>2</sub> gas sensing [68]. The researchers synthesized ZnO multilayer nanosheets and ZnO-In<sub>2</sub>O<sub>3</sub> nanocomposites using a hydrothermal method, followed by Ag nanoparticle modification through a chemical reduction process. Gas sensing tests demonstrated that the AgZO-In<sub>2</sub>O<sub>3</sub> sensor exhibited superior performance, including a significantly lower optimal operating temperature of 160°C, rapid response and recovery times, and enhanced sensitivity compared to unmodified ZnO-In<sub>2</sub>O<sub>3</sub> sensors. The enhanced performance was attributed to the increased specific surface area, enhanced oxygen adsorption, heterojunction formation, and catalytic effects of Ag nanoparticles.

Another approach to H<sub>2</sub> detection involves bimetallic Ag/Pd nanoparticle-functionalized ZnO nanoplates. The study by Nguyet et al. investigates the development of a high-performance H<sub>2</sub> gas sensor utilizing Ag/Pd nanoparticle-functionalized ZnO nanoplates [69]. The experimental approach involved synthesizing ultrathin ZnO porous nanoplates via a hydrothermal method and decorating them with bimetallic Ag nanoparticles, synthesized using a modified polyol technique. The prepared Ag/Pd-ZO nanoplates were drop-cast onto Pt interdigital electrodes and annealed to enhance sensor stability. The gas sensing properties were evaluated by exposing the sensor to H<sub>2</sub> concentrations ranging from 25 ppm to 500 ppm at varying temperatures. The findings revealed that the Ag/Pd-ZO sensors exhibited superior sensitivity, selectivity, and rapid response-recovery characteristics compared to pure ZnO sensors. The optimal sensor response was recorded at 350°C, demonstrating a significantly enhanced response time of 6s and high selectivity for H<sub>2</sub> over interfering gases.

To further enhance sensitivity, researchers have explored AgZO hollow microstructures for H<sub>2</sub> gas sensing applications. The study by Agarwal et al. investigates the development of a highly efficient H<sub>2</sub> gas sensor using AgZO hollow microstructures [70]. The gas sensing performance was tested at different temperatures and H<sub>2</sub> concentrations, revealing that the AgZO sensor demonstrated a remarkable 479% sensitivity enhancement compared to pure ZnO at 250°C for 300 ppm H<sub>2</sub> gas. The Ag nanoparticles enhanced H<sub>2</sub> adsorption through chemical and electronic sensitization, improving response time, recovery rate, and selectivity. The study found that AgZO sensors exhibited superior stability and repeatability over multiple cycles, with a significant preference for H<sub>2</sub> over CO and CO<sub>2</sub>.

Bimetallic nanoparticle functionalization has also been explored in ZnO nanorods to enhance H<sub>2</sub> sensing capabilities. The study by Kumar et al. investigates the H<sub>2</sub> sensing capabilities of ZnO nanorods decorated with bimetallic Ag/Pd nanoparticles [71]. The ZnO nanorods were synthesized using a hydrothermal method and subsequently functionalized with Ag and Pd nanoparticles via chemical reduction. The gas sensing experiments were conducted on interdigitated electrodes (IDEs) coated with Ag-Pd/ZnO, testing responses to various gases at different temperatures. The 1:1 Ag/Pd-ZnO composition exhibited the highest response of 51.36 to 100 ppm of H<sub>2</sub> at an optimized temperature of 275°C, significantly outperforming pure ZnO sensors. The enhanced performance was attributed to the synergistic effect of Ag/Pd nanoparticles, which enhanced electron transfer, provided additional reactive sites, and facilitated selective H<sub>2</sub> adsorption.

For applications requiring multifunctional sensing, AgZO single nanowires have demonstrated remarkable performance in H<sub>2</sub> detection. The study by Lupan et al. investigates the synthesis and characterization of AgZO single nanowires [72]. The researchers show casing significant improvements in sensitivity, response time, and recovery time compared to previous literature. The sensors exhibited a two-order increase in current under UV exposure and faster response times, making them ideal candidates for ultra-sensitive and low-power sensors. The experimental results

demonstrated that the doping of silver into ZnO nanowires enhanced H<sub>2</sub> gas sensing with fast response and recovery times of 22s, and high sensitivity to H<sub>2</sub> (50%) at room temperature. The study also proposed a sensing mechanism where Ag ions help ionize oxygen at the surface of the nanowires, enhancing their reactivity. This led to better electron-hole pair separation, improving the photodetector performance. Table 6 shows the parameters of sensors mentioned before.

**Table 6**  
Hydrogen sensing properties of Silver-doped ZnO sensors

| Structure              | Definition of Sensitivity | Concentration | Operating Temperature | Sensitivity | Response time | Ref  |
|------------------------|---------------------------|---------------|-----------------------|-------------|---------------|------|
| Nanoparticles          | $S = \frac{R_a}{R_g}$     | 100 ppm       | 160 °C                | 103.75      | 47.8 s        | [68] |
| Nanoplates             | $S = \frac{R_a}{R_g}$     | 500 ppm       | 350 °C                | 0.15        | 2 s           | [69] |
| Hollow microstructures | -                         | 300 ppm       | 250 °C                | 479 %       | -             | [70] |
| Nanorods               | $S = \frac{R_a}{R_g}$     | 100 ppm       | 275 °C                | 51.36       | -             | [71] |
| Single Nanowire        | $S = \frac{I_a}{I_g}$     | 100 ppm       | RT                    | 50 %        | 22 s          | [72] |

### 5.3 Pt-Doped ZnO Hydrogen Sensor

Pt significantly enhances H<sub>2</sub> gas sensing performance due to its strong oxygen dissociation, spillover effect, and synergic electronic interaction with oxide materials. Functionalizing semiconducting metal oxide sensors with noble metals like Pt enhances efficiency by breaking down H<sub>2</sub> gas molecules into reactive atomic hydrogen, which is then transported to the semiconductor surface via the spillover effect, accelerating the reaction between hydrogen and the host material [74, 75].

In the search for optimized H<sub>2</sub> sensing, the study by Kumar et al. investigates the effect of Pt nanoparticles on ZnO microstructures at reduced operating temperatures. The study by Kumar et al. focuses on optimizing the loading of Pt nanoparticles in ZnO microstructures to enhance H<sub>2</sub> gas sensing performance at a reduced working temperature of 150°C [75]. The researchers synthesized Pt-loaded ZnO (PtZO) pencil-like microstructures using a hydrothermal method. The gas sensors were fabricated by depositing PtZO onto interdigitated electrodes and tested for their response to H<sub>2</sub> gas and other interfering gases. The results indicated that ZnO sensors with % Pt exhibited the highest response (64% to 100 ppm) at 150°C, significantly outperforming pure ZnO sensors, which required 250°C for a minimal response. The PtZO sensors also demonstrated excellent repeatability, long-term stability, and high selectivity for H<sub>2</sub> gas compared to carbon monoxide, carbon dioxide, methene, ammonia, and ethanol. The enhanced sensing performance was attributed to Pt nanoparticles enhancing electronic sensitization, catalytic activity, and gas adsorption by modifying the ZnO surface properties. Additionally, Pt incorporation reduced ZnO grain size, increasing the number of active sites for gas interaction.

The role of Pt doping in enhancing ZnO's H<sub>2</sub> sensing properties is further explored in the study by Hastir et al. This research investigates the impact of Pt doping on ZnO's gas sensing performance, synthesized using a co-precipitation method [76]. ZnO and PtZO nanoparticles were synthesized using a co-precipitation method. The XRD analysis confirmed the hexagonal wurtzite structure of ZnO with successful Pt incorporation, while Raman spectroscopy indicated increased defects such as oxygen vacancies in doped samples. FESEM images revealed morphological differences, suggesting

that Pt doping altered nanoparticle growth. Gas sensing measurements demonstrated that the optimal operating temperature of ZnO sensors decreased from 400°C to 350°C upon Pt doping, with a significant increase in H<sub>2</sub> response, particularly in the 0.05% Pt-doped ZnO sample. This improvement was attributed to the catalytic properties of Pt, which facilitated enhanced surface reactions through a spill-over effect, as well as the increase in oxygen vacancies that promoted better gas adsorption and desorption.

High-temperature operation of H<sub>2</sub> sensors is also an important consideration. The study by Uddin et al. explores the fabrication and performance of platinum PtZO nanoparticle-based H<sub>2</sub> sensors designed for high-temperature operation of 300°C [77]. Using RF magnetron sputtering, ZnO nanoparticles were deposited on an Al<sub>2</sub>O<sub>3</sub> substrate, followed by rapid thermal annealing at different temperatures (800°C-1100°C) to optimize sensor morphology. Pt was then sputtered onto the ZnO surface to enhance catalytic activity. The gas sensing experiments revealed that the sensor demonstrated excellent stability, rapid response and recovery times, and reliable H<sub>2</sub> detection within a concentration range of 100-40,000 ppm. Among the tested sensors, the one annealed at 1000°C exhibited the best performance, showing a 14.9% response to 1000 ppm with response and recovery times of 133s and 112s, respectively. The sensor maintained its stability for 30 days with minimal degradation and showed resistance to humidity variations.

The study by Mokrushhin et al. investigates the gas-sensing properties of PtZO nanocomposites synthesized through a solvothermal method and applied as thin films using micro plotter printing [78]. The PtZO powders were prepared with varying platinum content. The films were tested for gas sensitivity towards H<sub>2</sub>, benzene, carbon monoxide, nitrogen dioxide, and ammonia, with electrical resistance measurements conducted under controlled atmospheric conditions. The results demonstrated that platinum doping significantly enhanced sensitivity to H<sub>2</sub> and benzene while reducing responses to carbon monoxide and nitrogen dioxide. This enhancement was attributed to the spillover effect and Schottky barrier formation at the PtZO interface, leading to increased catalytic activity and electronic sensitization. Among the tested compositions, ZnO films with 0.5-1 % Pt exhibited the highest response to H<sub>2</sub> and benzene, while further increasing platinum content to 3 % led to a slight decrease in sensitivity. Response times for H<sub>2</sub> (24-60 s) were notably shorter than for benzene (55-171 s), attributed to the rapid 30 hermos-catalytic reaction facilitated by platinum.

Lastly, research to enhanced H<sub>2</sub> sensing by Drmosh et al. presents an innovative approach to fabricating a platinum-loaded reduced graphene oxide (rGO)/ZnO hybrid nanocomposite for H<sub>2</sub> sensing [79]. Using pulsed laser ablation in liquid (PLAL) and direct current (DC) sputtering techniques, ZnO nanoparticles were synthesized and combined with rGO before Pt thin films were deposited to enhance sensor performance. The experimental findings highlight that the ternary rGO/PtZO sensor demonstrated superior sensitivity, selectivity, and stability compared to pure ZnO and rGO/ZnO counterparts. Structural and morphological characterizations confirmed the homogeneous dispersion of Pt nanoparticles, enhanced surface properties, and optimized charge transfer mechanisms, crucial for efficient gas sensing. The gas sensing experiments revealed that the sensor exhibited a high response of approximately 99% to 400 ppm H<sub>2</sub> at an optimal operating temperature of 100°C, outperforming other rGO-based gas sensors. The response time was fast, with good repeatability and long-term stability over 45 days. The study also investigated the gas sensing mechanism, demonstrating that Pt nanoparticles played a crucial role in enhancing H<sub>2</sub> adsorption, reducing activation energy, and facilitating charge transfer, leading to an efficient and low-power H<sub>2</sub> sensor. Table 7 shows the parameters of sensors mentioned before.

**Table 7**  
Hydrogen sensing properties of Platinum-doped ZnO sensors

| Structure     | Definition of Sensitivity                                 | Concentration | Operating Temperature | Sensitivity | Response time | Ref  |
|---------------|-----------------------------------------------------------|---------------|-----------------------|-------------|---------------|------|
| Pencil-like   | $S = \left[ \frac{ R_a - R_g }{R_a} \right] \times 100\%$ | 100 ppm       | 150 °C                | 63.8 %      | 193 s         | [75] |
| Spherical     | -                                                         | 250 ppm       | 350 °C                | 9           | 20 s          | [76] |
| Shaped        | -                                                         | -             | -                     | -           | -             | -    |
| Thin film     | $S = \frac{G_a - G_g}{G_a} \times 100$                    | 1000 ppm      | 300 °C                | 14.9 %      | 113 s         | [77] |
| Nanoparticles | $S = \frac{R_a}{R_g}$                                     | 100 ppm       | 250 °C                | 2           | 119 s         | [78] |
| Thin film     | $= \frac{R_a - R_g}{R_a} \times 100$                      | 400 ppm       | 180 °C                | 99 %        | 12 s          | [79] |

## 6. Conclusion

In conclusion, the creation of metal-doped ZnO nanostructures has demonstrated great promise for improving H<sub>2</sub> sensing capabilities by solving fundamental problems in sensitivity, selectivity, and stability. Researchers were able to increase sensor performance by introducing different dopants such as aluminium, magnesium, manganese, cobalt, and noble metals such as palladium, silver, and platinum. Sol-gel synthesis, hydrothermal growth, and chemical vapor deposition techniques have all played a role in the development of these sophisticated materials, with each providing distinct benefits in terms of scalability and control over nanostructure morphology. Despite advancements, issues with long-term stability, repeatability, and selectivity in real-world applications persist, demanding more research into hybrid nanomaterials, composite architectures, and enhanced doping techniques. This paper emphasizes the potential of metal-doped ZnO nanostructures to advance H<sub>2</sub> sensor technology, therefore making H<sub>2</sub>-based energy systems safer and more efficient, as well as environmental monitoring.

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