

REVIEW

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Advances in inorganic conductive material- and organic conductive polymer-based resistive gas sensors for room-temperature H₂S detection

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Abstract

Hydrogen sulfide (H₂S) is a colorless, flammable, and highly toxic gas that underscores the need for cost-effective, energy-efficient, simple, convenient, and durable detection methods. Resistive gas sensors based on inorganic conductive materials and organic conductive polymers can effectively address these requirements. This review discusses the hazards of H₂S gas and reviews sensors capable of detecting H₂S at room temperature, including those based on metal oxides, MXene/carbon materials, and p-type conductive polymers. It explores the mechanisms behind their enhanced response at room temperature, such as utilizing special structures (e.g., porous/hollow nanospheres, nanowires, nanotubes, and nanocapsules) to increase the effective surface area of the sensing materials, employing metal particles sensitization to improve gas adsorption, and leveraging heterojunctions to amplify the response. Additionally, this review highlights the limitations of these sensors and provides insights for the further development of low-power resistive H₂S gas sensors.

Keywords H₂S gas sensor, Room temperature, Response, Conductive polymer, Metal oxide

Introduction

H₂S is a highly fat-soluble, corrosive, toxic, and flammable gas with a distinct rotten egg odor. It commonly originates from human and animal waste, manufacturing industries, oil and mining extraction, and volcanic eruptions [1]. H₂S poses significant risks to human health, including damage to mucous membranes (e.g., eyes and throat) and inhibition of cellular respiration [2, 3]. Even at concentrations as low as a few hundred ppb, exposure for more than 10 min can impair the sense of smell and nervous system [4]. Furthermore, short-term exposure to concentrations exceeding 250 ppm can be fatal [5]. Therefore, real-time and accurate H₂S detection is essential to safeguard human health. Additionally, H₂S

is flammable and explosive at high temperatures, requiring stringent detection. Although methods such as electrochemiluminescence [6], fluorescent probes [7–9], and chemical techniques [10, 11] have been developed, their high costs and complex processes limit their practical application. Consequently, there is a growing demand for H₂S detection devices that are fast, highly sensitive, selective, simple, reusable, inexpensive, and portable for room-temperature operation. Chemiresistive gas sensors show great potential for satisfying these requirements.

The working principle of a chemiresistive gas sensor involves converting the interaction between the target analyte and sensing material (or oxygen molecules) into a change in electrical signal. The baseline is defined as the electrical signal measured under air or nitrogen (N₂) conditions. The key performance metrics for chemiresistive gas sensors include response magnitude (expressed as the percentage change in resistance or current relative to initial resistance or current), response/recovery time, selectivity, stability, and repeatability. The

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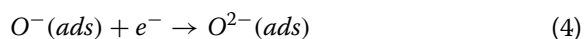
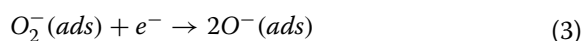
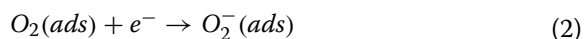
response/recovery time refers to the duration required for the sensor response to reach 90% of the total electrical signal change after exposure to the target gas or air (or N_2). Selectivity is defined as the difference between the responses of the target gas and interfering gases. The larger the difference, the more selective the sensor is.

Inorganic conductive materials and organic conductive polymers-based chemiresistive sensors have shown remarkable performance due to the diverse structure and geometries of sensing layer. This article reviews and discusses the performance of inorganic conductive material and organic conductive polymer-based H_2S gas sensors that are used at room temperature, focusing on sensing enhancement mechanism. While humidity can influence sensor responses owing to interactions between H_2S and H_2O molecules, this study primarily examined how the structure and geometry of the sensing layer affect performance. Consequently, the effect of humidity on the H_2S response was not explored in detail.

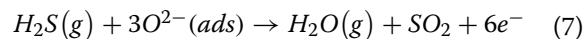
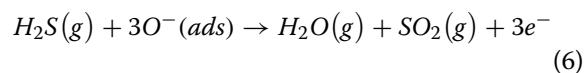
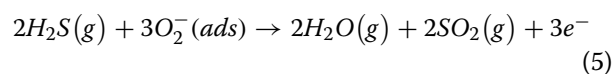
Inorganic conductive material-based sensors

Metal oxide-based sensors

Metal oxide-based sensors are widely used for gas detection because of their high sensitivity, low cost, and long-term stability. These include NO_2 [12–14], acetone [15, 16], ethanol [17, 18], volatile organic compound (VOC) [19, 20], H_2S [21, 22], and human biomarkers [23]. However, they typically require higher operating temperatures, which is attributed to the reaction mechanism of gas molecules on their surfaces. Taking H_2S gas as an example, in air, oxygen molecules adsorb onto metal oxide surfaces and extract electrons from their conduction bands to form O_2^- , O^- , and O^{2-} [21, 24], as shown in Eqs. 1–4.



When the sensor was exposed to H_2S gas, these gas molecules reacted with the adsorbed oxygen, releasing electrons back into the metal oxide, as described in Eqs. 5–7. However, the further dissociation of O_2^- into O^- and O^{2-} requires temperatures above 150 °C [22]. Consequently, metal-oxide-based sensors typically require high operating temperatures to enhance their responses.



To improve the response of metal oxide-based H_2S gas sensors at room temperature, researchers have explored various strategies, including increasing oxygen absorption sites, metal particles catalyze the decomposition of gas molecules, and utilize heterojunctions to enhance the potential barrier between the sensing materials. Increasing the effective surface area of the sensing material and sensitizing with metal particles are the key strategies for enhancing O_2 adsorption sites in the sensing layer. For sensors composed of a single conductive material, creating pores on the surfaces of nanoparticles or microspheres and assembling them into a sensing layer with high pore density is a key approach for increasing the effective surface area of the material.

The “grape”-structured sensor composed of copper oxide (CuO) nanoparticles (Fig. 1a) on a ceramic tube showed a detectable concentration range of 0.1 ppb to 1 ppm, a high response of 148 ($\Delta R/R_{air}$) at 1 ppm, approximately 200/1000 s of response/recovery time, three cycles of reproducibility at 0.5 ppb, excellent selectivity, and a detection limit as low as 0.1 ppb. The gaps between the CuO nanoparticles provide channels for H_2S gas diffusion and increase the effective area of the sensing material. However, there are no reports on its long-term stability [25]. Similarly, a sensor fabricated by coating porous iron oxide ($\alpha\text{-Fe}_2O_3$) nanoparticles on a ceramic tube (Fig. 1b) demonstrated a detectable concentration range of 0.05–100 ppm, a detection limit of 50 ppb, a high response of 1.1/38.4 (R_{air}/R_{gas}) at 0.05/100 ppm, excellent selectivity, and 4 cycles of repeatability at 1 ppm [26]. Additionally, the sensor prepared by screen-printing sponge-like loose porous tin oxide (SnO_2) microspheres and adhesive on an alumina ceramic chip showed a detectable concentration range of 0.1–10 ppm, a response of up to 9688 (R_{air}/R_{gas}) to 10 ppm H_2S , a fast response/recovery time of 5/177 s, 3 cycles of repeatability at 10 ppm, high selectivity, and stability that can be maintained for more than one month. However, ambient humidity must be kept at a relative humidity of $50 \pm 5\%$ to maintain these excellent properties [27].

Metal particle sensitization enhances target gas response in sensing materials by promoting gas molecule decomposition, increasing surface activity, and facilitating carrier transfer. For example, in situ-grown, etched, and tungsten-doped zinc oxide (ZnO) nanotubes (EW-ZnO NTs) deposited on fluorine-doped tin oxide (FTO)

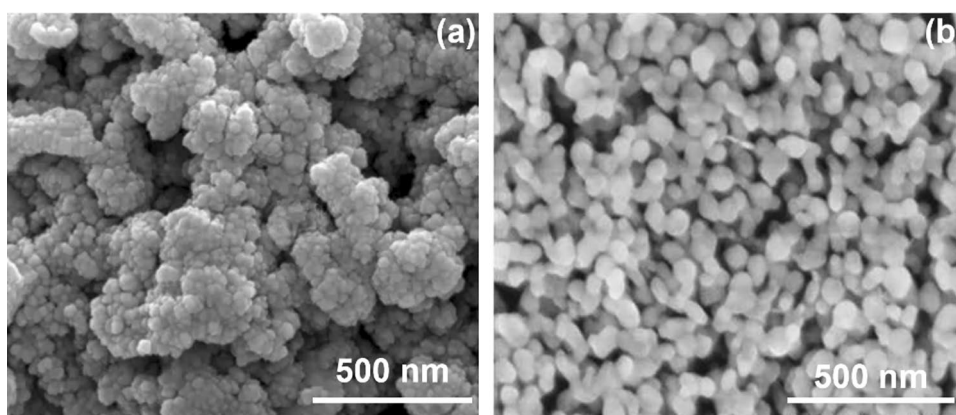


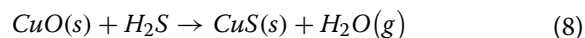
Fig. 1 SEM image of **a** "grape"-like CuO [25] and **b** α -Fe₂O₃ [26]. Reproduced with permission from [25], Copyright 2019 Elsevier. Reproduced with permission from [26], Copyright 2015 Elsevier

electrodes increased the oxygen adsorption sites via the platinum (Pt) sensitization. Additionally, the Schottky barrier formed between Pt and EW-ZnO amplified the resistance difference of the sensor before and after H₂S sensing. Consequently, the sensor showed a detection range of 0.1–30 ppm, a high response of 1.25/70 ($R_{\text{air}}/R_{\text{gas}}$) at 0.1/30 ppm, response/recovery times of 165/95 s, repeatability over 5 cycles at 10 ppm, excellent selectivity, and maintained stability over 30 days at room temperature for H₂S detection [28]. Similarly, gold nanoparticle (AuNP)-sensitized SnO₂ demonstrated a detection range from 2 ppb to 500 ppm, a response of 0.001/2.5 ($\Delta I/I_{\text{air}}$) at 2 ppb/500 ppm, and response/recovery times of 30/126 s. This sensor also showed good selectivity and repeatability over 12 cycles at 0.05 ppm, although stability data were not provided [29].

The heterojunction creates a potential barrier between different materials, thereby increasing the sensor's initial resistance. In ambient air, oxygen molecules adsorb on the surface and capture electrons, forming a depletion layer that further elevates the resistance. However, when exposed to H₂S, a reaction occurs between H₂S and the adsorbed oxygen, releasing electrons and consequently lowering the sensor's resistance. Based on this mechanism, manganese dioxide (MnO₂) nanoparticle-modified molybdenum trioxide (MoO₃) nanobelts demonstrated an impressive detection range of 0.1–100 ppm, with a response of 1.5/35 ($R_{\text{air}}/R_{\text{gas}}$) at 0.1/100 ppm, response/recovery times of 40/42 s, repeatability over 5 cycles at 1 ppm, excellent selectivity, and stability maintained for 50 days [30]. Similarly, multilayer titanium carbide (Ti₃C₂T_x)-intercalated α -Fe₂O₃ exhibited a detection range of 0.3–100 ppm, a response of 1/20 ($R_{\text{air}}/R_{\text{gas}}$) at 0.3/100 ppm, and response times ranging from 50 to 600 s. This sensor also demonstrated good repeatability

over 4 cycles at 100 ppm, along with selectivity and stability for 10 days, although the recovery time was not reported [31]. In addition, a heterojunction composed of Fe₂O₃ and Ti₃C₂T_x-derived TiO₂ displayed a detection range of 0.2–50 ppm, with responses of 0.1/0.75 ($\Delta R/R_{\text{air}}$) at 10/50 ppm, response/recovery times of 228/1400 s, and repeatability over 3 cycles at 10 ppm, all while maintaining a good selectivity and a stability for 10 days [32]. Furthermore, the n–n junction formed between tungsten trioxide (WO₃) and bismuth tungstate (Bi₂WO₆) enabled a sensor to achieve a detection range of 2–100 ppb, with a response of 1.13/7.86 ($R_{\text{air}}/R_{\text{gas}}$) at 2/100 ppb, response/recovery times of 52/119 s, and excellent repeatability over 24 cycles at 40 ppb, in addition to selectivity and stability for 7 days [33]. Lastly, the p–n junction between indium oxide (In₂O₃) and molybdenum disulfide (MoS₂) resulted in the In₂O₃/MoS₂-based sensor exhibited a detectable concentration range from 5 ppb to 50 ppm, a response of 4 at 5 ppb and 460.61 ($R_{\text{air}}/R_{\text{gas}}$) at 50 ppm, response and recovery times ranging from 84 to 490 s and 380 to 1977 s respectively, repeatability over 4 cycles at 50 ppm, and reliable selectivity and stability for 14 days [34].

It is worth noting that the mechanism by which p–n junctions enhance the response of CuO-containing sensors to H₂S gas involves not only the modulation of sensor resistance by the p–n junction but also the reaction between p-type CuO and H₂S gas, as illustrated in Eq. 8.



When p-type CuO comes in contact with a n-type semiconductor material in air, electrons from the n-type material flow into CuO, whereas holes flow from CuO to the n-type material until the Fermi level reaches

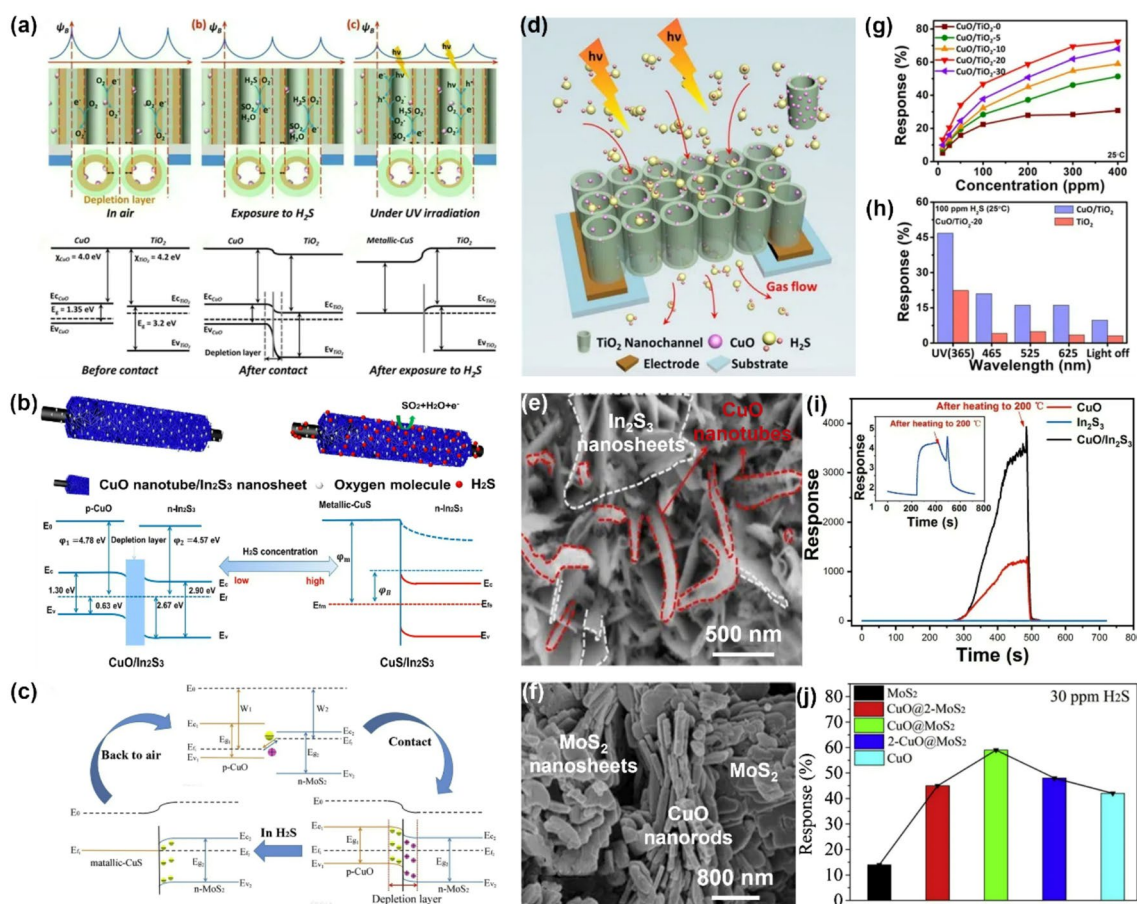


Fig. 2 Response mechanism of the **a** CuO/TiO₂- [36], **b** CuO/In₂S₃- [37], and **c** CuO/MoS₂-based sensors to H₂S gas [38]. Sensing layer structures of **d** CuO/TiO₂- [36], **e** CuO/In₂S₃- [37], and **f** CuO/MoS₂-based H₂S gas sensors [38]. **g** Relationship between gas response and H₂S concentrations of pristine TiO₂- and CuO/TiO₂-based gas sensors. The concentration range is 10–400 ppm [36]. **h** Comparison of 100 ppm H₂S gas response between pristine TiO₂- and CuO/TiO₂-based sensors under light irradiation with varying wavelengths [36]. **i** Comparison of 50 ppm H₂S gas response between pristine CuO-, In₂S₃-, and CuO/In₂S₃-based sensors with different In₂S₃ sputtering times [37]. **j** Comparison of 30 ppm H₂S gas response between pristine CuO- and CuO/MoS₂-based sensors with different CuO/MoS₂ concentration ratios [38]. Reproduced with permission from [36], Copyright 2021 American Chemical Society. Reproduced with permission from [37], Copyright 2021 American Chemical Society. Reproduced with permission from [38], Copyright 2019 Elsevier

equilibrium. This interaction forms a depletion layer between the n-type semiconductor and CuO, causing the overall resistance to be higher than that of pure CuO or pure n-type semiconductors. When H₂S gas is introduced, the H₂S molecules react with the adsorbed oxygen ions, releasing electrons (Eqs. 5–7) and reducing the thickness of the depletion layer between CuO and the semiconductor material, thereby lowering sensor resistance. Simultaneously, a reaction between CuO and H₂S occurs, forming copper sulfide (CuS) (Eq. 8). CuS, a metallic material with excellent electrical conductivity [35], can replace CuO in p–n junctions. Consequently, the p–n junction between CuO and the semiconductor material is gradually substituted by a Schottky barrier between

CuS and the semiconductor material, further decreasing the resistance of the device.

As shown in Fig. 2a, d, the sensor fabricated by coating p-type CuO nanoparticles onto independent titanium dioxide (TiO₂) (n-type) nanochannels has a large surface area and forms a p–n junction. Compared with the pristine TiO₂-based sensor, the CuO/TiO₂-based sensors showed significantly enhanced responses in the H₂S gas concentration range of 10–400 ppm, as seen in Fig. 2g. This sensor achieved a detection range of 3–400 ppm, a response/recovery time of 41/92 s, excellent selectivity, 5 cycles of reproducibility at 100 ppm, and stability for up to 60 days. However, it only showed a response of approximately 70% ($\Delta R/R_{\text{air}}$) at a high

concentration of 400 ppm. Moreover, these excellent properties require 365 nm LED illumination to maintain. This is attributed to the promoting effect of LED lighting on oxygen adsorption/desorption and CuS reoxidation (Fig. 2h). Additionally, the sensor utilizes PDMS as a substrate, enabling consistent H₂S sensing performance even under bending (from flat to 6 mm radius) and vertical/lateral stretching conditions [36]. Similarly, the sensor fabricated by sputtering n-type indium sulfide (In₂S₃) onto p-type CuO nanotubes on ceramic tubes featured both a large surface area and a p–n junction, as shown in Fig. 2b, e. CuO/In₂S₃-based sensor demonstrated a detectable concentration range of 10–60 ppm, excellent selectivity, stability for up to 30 days, and an impressive 3511 ($R_{\text{air}}/R_{\text{gas}}$) response to 50 ppm H₂S gas. Although the CuO/In₂S₃-based sensor showed significantly enhanced response, its recovery is very poor and requires the application of pulsed current to heat the sensor to 200 °C for complete recovery, as shown in Fig. 2i. This limitation arises from the reduced ability of the metal oxide surface to desorb oxygen and reoxidize CuS to CuO at room temperature, requiring additional energy inputs such as light or heat. Consequently, the 3-cycle reproducibility exhibited by this sensor at 50 ppm also depends on the pulsed current heating [37]. Additionally, a p-CuO nanorod/n-MoS₂ nanosheet-based sensor was assembled layer-by-layer on the FR4 substrate (Fig. 2c, f) and exhibited a higher response than the pristine CuO- and MoS₂-based sensors (Fig. 2j). The CuO/MoS₂-based sensor exhibited a response range of 1 ppb–100 ppm for H₂S gas, an extremely low detection limit of 1 ppb, a response/recovery time of 38/102 s, excellent selectivity, 30 days of stability, and approximately 80% ($\Delta R/R_{\text{air}}$) response at 100 ppm. The sensor demonstrated excellent reproducibility over 4 cycles at each concentration (0.5, 10, and 30 ppm). These excellent properties are attributed to the synergistic effect of the p–n junction and large effective surface area [38]. In addition, p-type CuO-functionalized n-type zinc ferrites (ZnFe₂O₄) demonstrated a detectable range of 0.1–100 ppm, with a response of 0.11/0.87 ($\Delta R/R_{\text{air}}$) at 0.1/100 ppm and response/recovery times of 70/475 s. The sensor also exhibited excellent reproducibility over 5 cycles at each concentration of 0.1, 1, and 10 ppm, along with high selectivity and stability maintained for 28 days [39].

MXene/carbon-based sensors

MXenes and carbon-based materials have been developed as gas sensors because of their metallic conductivity and semiconducting properties. However, the sparse oxygen adsorption sites on their surfaces limit their

application as H₂S gas sensors. To solve this problem, it is necessary to sensitize these materials with metal particles to provide more adsorption sites for oxygen molecules and to catalyze the cracking of H₂S gas.

A Ti₃C₂T_x MXene sensor sensitized with silver nanoparticles (AgNPs) on a silicon wafer showed an enhanced response compared with that of a pristine Ti₃C₂T_x-based sensor (Fig. 3a). As shown in Fig. 3b, this improved response is due to the catalytic effect of AgNPs on surface O₂ adsorption/desorption and the strong interaction between Ag and S atoms. AgNPs/Ti₃C₂T_x-based sensor demonstrated a detectable concentration range of 0.05–10 ppm, a theoretical detection limit of 35 ppb, a response of 60% ($\Delta I/I_{\text{air}}$) at 10 ppm, a response/recovery time of 34/58 s, selectivity, 10 cycles of reproducibility at 1 ppm, and 20 days of stability. Notably, this study developed a calibration strategy for the quantitative detection of H₂S by plotting the sensor response versus the H₂S concentration at each relative humidity (5–80%). However, the sensor recovery is not satisfactory [40]. Based on a similar enhancement mechanism, graphene (G) modified with AgNPs and charged impurities on silicon wafers exhibited a higher response than pristine graphene, AgNP-doped graphene, and charged impurity-doped graphene, as shown in Fig. 3c. As a result, the sensor showed a detection range of 0.5–50 ppm, a response ($\Delta R/R_{\text{air}}$) of 37/137% at 0.5/50 ppm, and selectivity for H₂S gas. However, the sensor requires hot air purge to aid recovery after reaction. Other properties of the sensor were not reported in this study [41]. Cu nanoparticle-modified single-walled carbon nanotube (SWCNT) exhibited a detection range of 5–150 ppm, a response/recovery time of 10/15 s, selectivity, and 30 days of stability. This was attributed to the catalytic effect of Cu nanoparticles on the cleavage of H₂S molecules. However, the sensor only showed approximately 70% response ($\Delta R/R_{\text{air}}$) at a high concentration of 150 ppm. Notably, the sensor with a PET substrate showed 6 cycles of excellent reproducibility under 20 ppm at a bending radius of 7.8 mm [42].

Organic conductive polymer-based sensors

Organic conductive polymers represented by polyaniline (PANI), poly(3,4-ethylenedioxythiophene) (PEDOT), and polypyrrole (PPy) have attracted widespread attention in the field of gas sensors due to their advantages such as light weight, low operating temperature, short response time, and high freedom in material design [43, 44]. PANI is widely used to prepare room-temperature H₂S gas sensors [43] owing to its tunable conductivity, simple acid/base doping characteristics, good mechanical properties, and ease of synthesis. PANI conductivity depends on its oxidation-protonation state. This can be

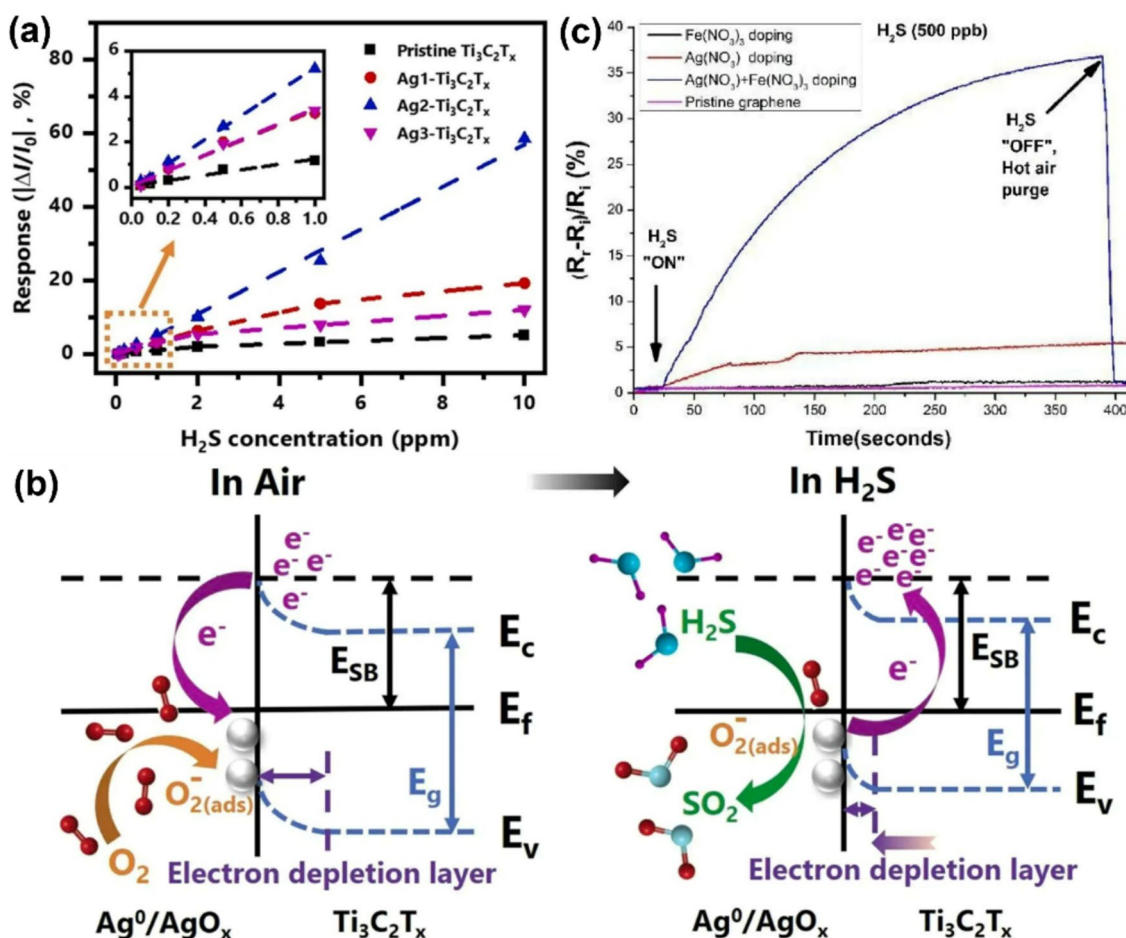


Fig. 3 **a** Comparison of H_2S gas response between pristine $Ti_3C_2T_x$ - and AgNPs/ $Ti_3C_2T_x$ -based sensors at a concentration range of 0.05–10 ppm [40]. **b** Response mechanism of the AgNPs/ $Ti_3C_2T_x$ -based sensor to H_2S gas [40]. Reproduced with permission from [40], Copyright 2022 Elsevier. **c** Comparison of H_2S gas response between pristine graphene-, AgNPs-doped graphene-, charged impurities-doped graphene-, and AgNPs/charged impurities-doped graphene-based sensors at a concentration of 0.5 ppm [41]. Reproduced with permission from [41], Copyright 2018 Elsevier

controlled by using alkali/acid solutions to provide protons for PANI doping. Commonly used dopants include hydrochloric acid (HCl), sulfuric acid (H_2SO_4), and water-dispersed polymeric acids. Water-dispersible polymeric acids, such as poly(4-styrene sulfonic acid) (PSS), poly(acrylic acid) (PAA), polyvinyl sulfonic acid (PVSA), and poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPSA)-doped PANI nanostructures exhibit good stability but poor conductivity [45]. This typically requires the addition of other fillers to enhance conductivity. Pernigraniline (fully reduced state), emeraldine (intermediate oxidation state), and leucoemeraldine (fully oxidized state) are the three most-studied oxidation and protonation states [46]. Pernigraniline and leucoemeraldine behaved as insulators, whereas emeraldine exhibited conductivity. Emeraldine is the most widely used state in resistive sensor, and it is considered to exhibit p-type semiconductor properties. When exposed to H_2S gas,

part of its structure is protonated, as shown in Eq. 9 [47]. This results in a decrease in PANI resistance. However, the structures in PANI that can be protonated by H_2S molecules account for only a small portion, and there are insulating structures that are not protonated by the dopants. This results in a limited sensing response. The incorporation of nanosensing materials into PANI has become the primary method for solving this problem.



Nanofibers based on camphor sulfonic acid (HCSA)-doped polyaniline-polyethylene oxide (PANI-PEO) rely solely on the reaction of PANI and H_2S and exhibit a response range of 1–10 ppm, response/recovery times of 120/250 s, good selectivity, and 45 days of stability. However, it showed only a 25% ($\Delta R/R_{air}$) response at 10 ppm. This is attributed to the limited protonation

ability of PANI and the barrier effect on the carrier transfer of undissolved PANI precursor substances during the synthesis process and PEO, which was used as a binder between the nanofibers. In summary, these materials are insulators [47]. To overcome this problem, other researchers have inserted graphene sheets into PSS-doped PANI to improve the electron-transfer capability of the sensor. As expected, the H_2S response of the PSS-doped PANI/graphene-based sensor was enhanced in the concentration range of 1–50 ppm. In addition to the reinforcement effect of graphene, the sulfonate anion ($-\text{SO}_3^-$) cleaved from H_2SO_4 used in the PANI synthesis process also attracts more H_2S molecules due to the existence of hydrogen bonds. Under this influence, the PSS-doped PANI/graphene sensor exhibited a response range of 1–50 ppm, a 20–80% ($\Delta R/R_{\text{air}}$) response at a concentration range of 1–50 ppm, a response/recovery time of 90/150 s, 5 cycles of reproducibility at 50 ppm, and good selectivity [45]. Similarly, when Ag clusters were synthesized within PANI, they enhanced the carrier transfer capability of the sensor and increased its ability to attract H_2S molecules. As illustrated in Fig. 4a, the synthesized Ag clusters were bound tightly to PANI, acting as active sites and carrier transfer channels. With an increase in the number of Ag clusters synthesized from AgNO_3 , the response of the PANI/Ag aggregate sensor to H_2S gas initially improved but later diminished (Fig. 4b). This decline was attributed to excessive Ag clusters, which reduced the effective surface area of PANI available for the response. The addition of an appropriate amount of Ag clusters enabled the sensor to exhibit a response of 450% ($\Delta I/I_{\text{air}}$, 25 ppm), a detectable concentration range of 1–25 ppm, and good selectivity. Unfortunately, there are no reports on other properties [48].

Additionally, some researchers have inserted metal oxides into PANI to improve the electron-transfer capability of the sensor. Simultaneously, these metal oxides can participate in reactions with H_2S and PANI to improve the response. As shown in Fig. 5a–c, the PANI nanocapsule/ ZnO sensor exhibited an improved response to H_2S gas by increasing the effective surface area of the sensor and forming a p–n junction. A depletion layer is formed between the p-type PANI and n-type ZnO owing to Fermi level alignment. In air, O_2 molecules capture electrons from ZnO , broadening the depletion layer and increasing resistance. When H_2S gas is introduced, the gas molecules react with the abundant oxygen ions in ZnO , releasing electrons and interacting with PANI to generate holes. This narrowed the depletion layer and decreased resistance. The sensor demonstrated a response range of 0.1–100 ppm, a response/recovery time of 63/12 s, 5 cycles of good reproducibility at each concentration (1, 5, and 30 ppm), and good selectivity. However, the response at higher concentrations (100 ppm) was limited to 53.5% ($\Delta R/R_{\text{air}}$) [49]. Based on this, the researcher proposed a p–n–p junction structure. As shown in Fig. 5d, e, a p–n junction was formed between the p-type rGO and the n-type SnO_2 hollow sphere attached to it. Simultaneously, the p-type PANI attached to SnO_2 formed another set of p–n junctions with SnO_2 . The synergy of multiple groups of p–n junctions successfully improved $\text{SnO}_2/\text{rGO}/\text{PANI}$ -based sensor response to H_2S (Fig. 5f). The p–n–p junction composed of three materials enables the sensor to exhibit a response of 3.18–91.11% ($\Delta R/R_{\text{air}}$) at a concentration of 0.05–10 ppm, a response/recovery time of 80–82/78–88 s, and a response/recovery range of 0.1–5 ppm, good selectivity, 30 days of stability, and 5 cycles of excellent

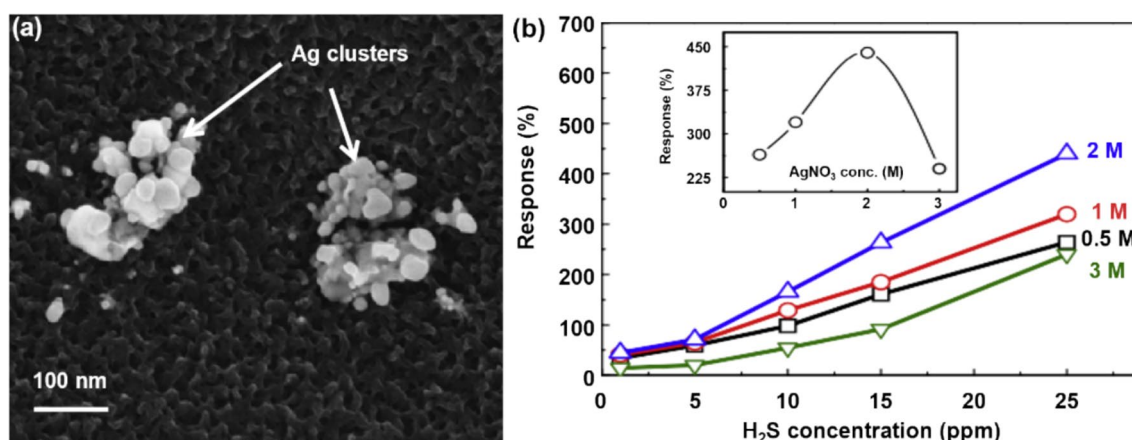


Fig. 4 **a** Sensing layer structures of the PANI/Ag clusters-based gas sensor [48]. **b** Comparison of H_2S gas response of the PANI/Ag cluster-based gas sensor with different AgNO_3 contents at H_2S concentration range of 1–25 ppm. Inset shows the response of PANI/Ag clusters prepared with different AgNO_3 concentrations at 25 ppm of H_2S gas [48]. Reproduced with permission from [48], Copyright 2014 Elsevier

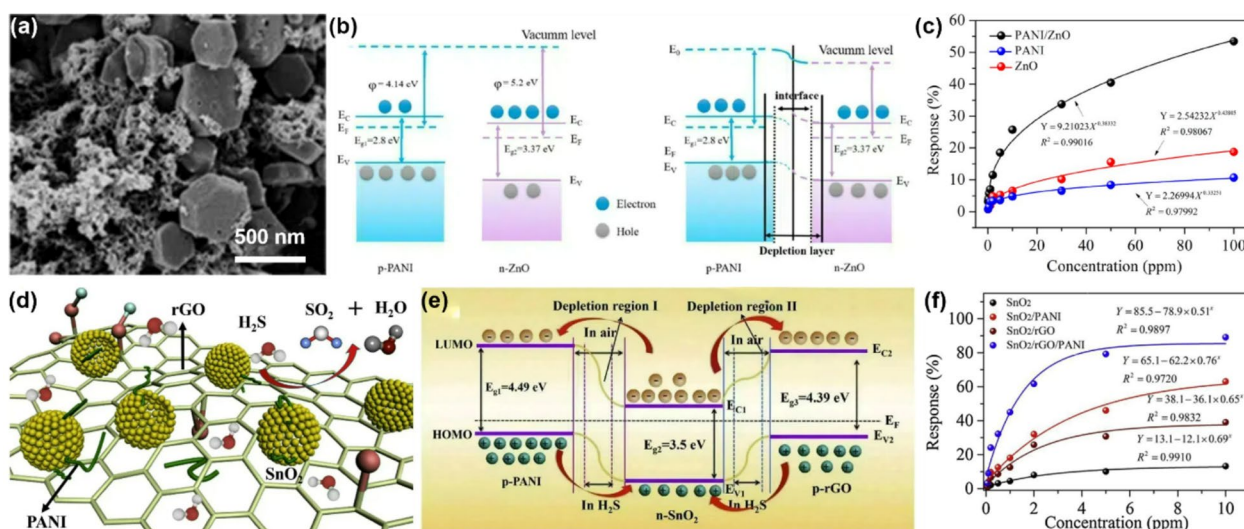


Fig. 5 Sensing layer structure of the **a** PANI nanocapsule/ZnO-based gas sensor [49] and **d** PANI/rGO/SnO₂-based gas sensor [50]. Sensing mechanism of the **b** PANI nanocapsule/ZnO-based gas sensor [49] **e** SnO₂/rGO/PANI-based gas sensor [50]. **c** Comparison of H₂S gas response between pristine PANI nanocapsule-, ZnO-, and PANI nanocapsule/ZnO-based gas sensor at a concentration range of 0.1–100 ppm [49]. **f** Comparison of H₂S gas response between pristine SnO₂-, SnO₂/PANI-, SnO₂/rGO-, and PANI/rGO/SnO₂-based gas sensors at a concentration range of 0.05–100 ppm [50]. Reproduced with permission from [49], Copyright 2019 American Chemical Society. Reproduced with permission from [50], Copyright 2019 Elsevier

reproducibility at different concentrations (0.1, 1, and 5 ppm) [50].

Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) and PPy are widely used as conductive carriers, sharing similarities with PANI in terms of improving conductivity through oxidative doping and exhibiting p-type semiconductor properties. Because PEDOT is insoluble in water, negatively charged PSS was added as a counter ion to enhance its water solubility. PPy, like PANI, features a π -conjugated structure that facilitates carrier transport. Compared with PANI, PEDOT:PSS offers superior flexibility and film-forming properties, whereas PPy exhibits good chemical stability in the atmosphere but suffers from brittleness and limited mechanical strength. Despite these differences, both materials exhibit conductivities comparable to that of PANI, leading researchers to combine them with inorganic conductive materials to develop advanced gas sensors [51, 52].

Cu_xO-polypyrrole aerogels doped with a graphene oxide (GO) skeleton leverage the microchannels and large surface area of the GO framework to provide numerous adsorption sites for gas molecules. The H⁺ ions generated from the H₂S decomposition interact with the p-type PPy, reducing sensor resistance. Simultaneously, H₂S reacts with Cu_xO to form Cu_xS, further enhancing its conductivity. The sensor demonstrated a response range of 2–200 ppm, good selectivity, and stability over 32 days. Additionally, when the H₂S gas concentration increased

from 2 to 200 ppm, the response and recovery times of the sensor increased from ~20 to ~300 s. However, specific response values have not been clearly reported [53]. The Cu²⁺-doped SnO₂ nanograin/PPy nanosphere sensor demonstrated a significantly enhanced H₂S gas response (Fig. 6a, b) and exceptional performance, attributed to the p–n junction formation between SnO₂ and PPy, as well as the Cu²⁺-induced enhancement of oxygen vacancies. The key features include a response range of 0.05–180 ppm, responses of 4/85 ($\Delta I/I_{\text{air}}$) at 0.05/50 ppm, 7/14 s of response/recovery time, selectivity, five cycles of excellent reproducibility at different concentrations (2 and 50 ppm), and stability over 32 days. Additionally, the sensor exhibited response and recovery times of just a few tens of seconds within the 0.3–50 ppm concentration range [51]. A sensor fabricated by sequentially depositing the AgNW film, graphene film, and PEDOT:PSS layer demonstrated an alternative design, as illustrated in Fig. 6c. Upon exposure to H₂S, the gas reacts with the AgNWs in the bottom layer to form Ag₂S, increasing sensor resistance. Additionally, H₂S doping made the PEDOT:PSS acidic, further corroding AgNWs and contributing to an increase in resistance. This is the primary factor contributing to the significantly enhanced response of the AgNW/PEDOT:PSS-based sensor to H₂S gas, as shown in Fig. 6d. The hygroscopic nature of PSS in the top PEDOT:PSS layer absorbs moisture, reducing the oxidation rate of the AgNWs and enhancing sensor stability. The sensor exhibited a response range

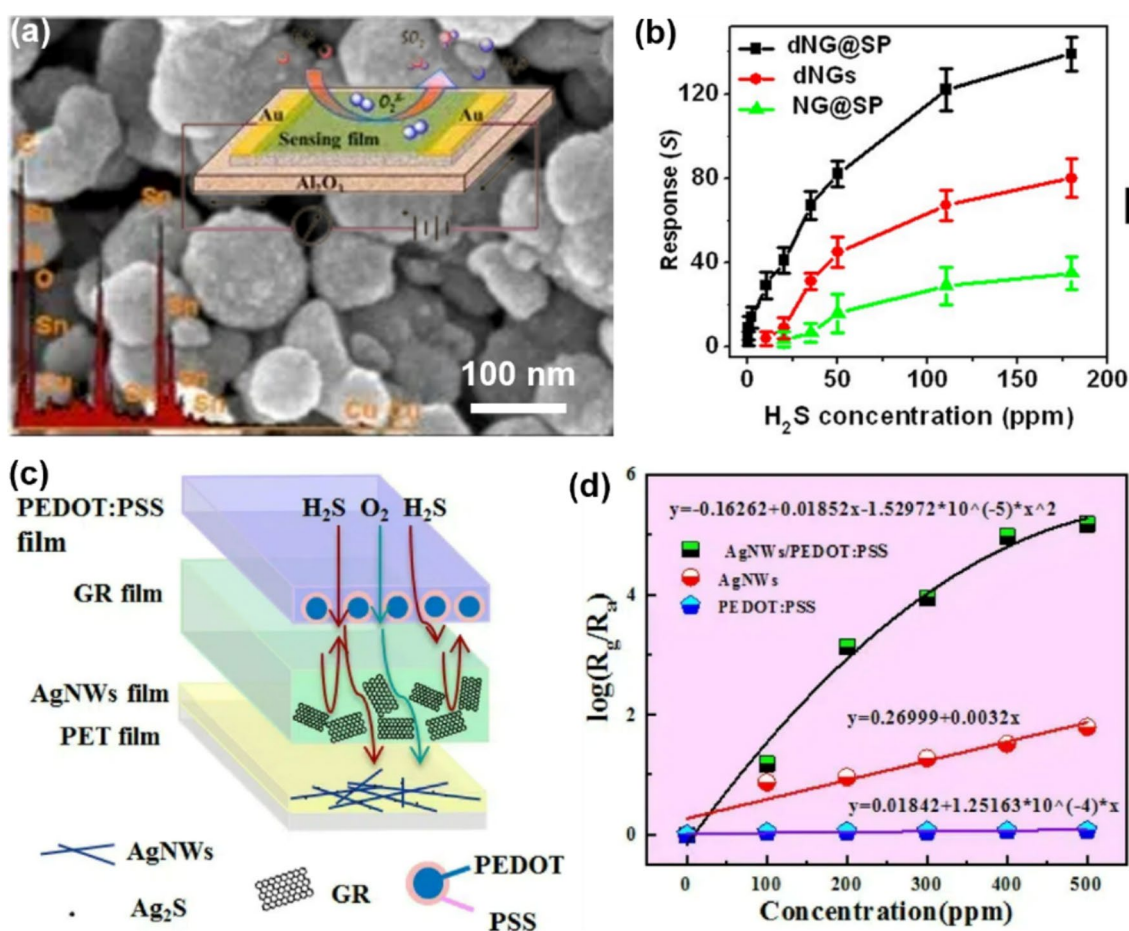


Fig. 6 Structure of the **a** Cu^{2+} -doped SnO_2 nanograin/PPy nanospheres-based sensor [51] and **c** PEDOT:PSS/graphene/AgNWs-based gas sensor [54]. **b** Comparison of H_2S gas response between pristine Cu^{2+} -doped SnO_2 nanograin (dNGs)-, SnO_2 nanograin/PPy nanosphere (NG@SP)-, and Cu^{2+} -doped SnO_2 nanograin/PPy nanospheres (dNG@SP)-based gas sensors at a concentration range of 0.05–180 ppm [51]. **d** Comparison of H_2S gas response between pristine PEDOT:PSS-, AgNWs-, and AgNWs/PEDOT:PSS-based gas sensors at a concentration range of 100–500 ppm [54]. Reproduced with permission from [51], Copyright 2017 American Chemical Society. Reproduced with permission from [54], Copyright 2021 American Chemical Society

of 100–500 ppm, responses of 15.1 and 149,466.7 ($R_{\text{air}}/R_{\text{gas}}$) at 100 and 500 ppm, respectively, and stability over 30 days. However, their reproducibility and selectivity remained unknown [54].

Conclusion and outlook

This article reviews strategies for improving the performance of inorganic conductive material- and organic conductive polymer-based chemiresistive H_2S gas sensors under room temperature. The main points include:

1. Sensing mechanism

H_2S interacts with adsorbed oxygen on the inorganic conductive material's surface, leading to the release of electrons. Or doping the organic conductive poly-

mer matrix releases the H^+ ions. This carrier modulation induces significant resistance changes, directly influencing sensor performance.

2. Structural optimization

Advanced nanostructures, such as porous or hollow nanospheres, nanowires, nanotubes, and nanocapsules, can significantly increase the effective surface area of the sensing materials and thus increase the oxygen adsorption sites. These structures also form microchannels that facilitate H_2S diffusion and enhance reaction kinetics, thereby improving sensor responsiveness.

3. Metal sensitization and catalysis

Incorporating metal particles (e.g., Ag, Cu) into the sensor material enhances oxygen adsorption, promotes carrier transfer, and catalyzes the dissociation of H_2S . This boosting the sensor's response.

Table 1 Performance of inorganic conductive material- and organic conductive polymer-based sensors at room temperature

Ref.	Material	Resp. formula	Response (%)	Conc. range (ppm)	Resp./Rec. time (s)	Reproducibility	Selectivity	Stability
[25]	CuO	$\Delta R/R_{\text{air}}$	14,800 (1 ppm)	0.0001–1	200/1000	3 cycles (0.5 ppm)	Yes	NA
[26]	$\alpha\text{-Fe}_2\text{O}_3$	$R_{\text{air}}/R_{\text{gas}}$	110 (0.05 ppm) 3840 (100 ppm)	0.05–100	120–440/100–3750	4 cycles (1 ppm)	Yes	NA
[27]	Sponge like SnO_2	$R_{\text{air}}/R_{\text{gas}}$	968,800 (10 ppm)	0.1–10	5/177	3 cycles (10 ppm)	Yes	> 30 days
[28]	In situ Pt/EW-ZnO	$R_{\text{air}}/R_{\text{gas}}$	125 (0.1 ppm) 7000 (30 ppm)	0.1–30	165/95	5 cycles (10 ppm)	Yes	30 days
[29]	Au/ SnO_2	$\Delta I/I_{\text{air}}$	1.1 (0.002 ppm) 250 (500 ppm)	0.002–500	30/126	12 cycles (0.05 ppm)	Yes	NA
[30]	MnO_2 decorated MoO_3 nanobelts	$R_{\text{air}}/R_{\text{gas}}$	150 (0.1 ppm) 3500 (100 ppm)	0.1–100	40/42	5 cycles (1 ppm)	Yes	50 days
[31]	$\alpha\text{-Fe}_2\text{O}_3/\text{Ti}_3\text{C}_2\text{T}_x$	$R_{\text{air}}/R_{\text{gas}}$	100 (0.3 ppm) 2000 (100 ppm)	0.3–100	50–600/NA	4 cycles (100 ppm)	Yes	10 days
[32]	$\text{Fe}_2\text{O}_3/\text{Ti}_3\text{C}_2\text{T}_x$ derived TiO_2	$\Delta R/R_{\text{air}}$	10 (0.2 ppm) 75 (50 ppm)	0.2–50	228/1400	3 cycles (10 ppm)	Yes	10 days
[33]	$\text{WO}_3\text{-Bi}_2\text{WO}_6$	$R_{\text{air}}/R_{\text{gas}}$	112.5 (0.002 ppm) 786 (0.1 ppm)	0.002–0.1	52/119	24 cycles (0.04 ppm)	Yes	7 days
[34]	$\text{In}_2\text{O}_3/\text{MoS}_2$	$R_{\text{air}}/R_{\text{gas}}$	400 (0.005 ppm) 46,061 (50 ppm)	0.005–50	84–490/380–1977	4 cycles (50 ppm)	Yes	14 days
[36]	p-CuO/n- TiO_2 nanochannels	$\Delta R/R_{\text{air}}$	70 (400 ppm)	3–400	41/92	5 cycles (100 ppm)	Yes	60 days
[37]	p-CuO/n- In_2S_3 nanotubes	$R_{\text{air}}/R_{\text{gas}}$	351,100 (50 ppm)	10–60	NA	3 cycles (50 ppm)	Yes	30 days
[38]	p-CuO nanorod/n- MoS_2 nanosheet	$\Delta R/R_{\text{air}}$	80 (100 ppm)	0.001–100	38/102	4 cycles (0.5, 10, 30 ppm)	Yes	30 days
[39]	CuO functionalized ZnFe_2O_4 porous spheres	$\Delta R/R_{\text{air}}$	10.8 (0.1 ppm) 87 (100 ppm)	0.1–100	70/475	5 cycles (0.1, 1, 10 ppm)	Yes	28 days
[40]	AgNPs/ $\text{Ti}_3\text{C}_2\text{T}_x$	$\Delta I/I_{\text{air}}$	60 (10 ppm)	0.05–10	34/58	10 cycles (1 ppm)	Yes	20 days
[41]	AgNPs/charged impurities-doped graphene	$\Delta R/R_{\text{air}}$	37 (0.5 ppm) 137 (50 ppm)	0.5–10	NA	NA	Yes	NA
[42]	Cu-modified SWCNT	$\Delta R/R_{\text{air}}$	70 (150 ppm)	5–150	10/15	6 cycles (20 ppm, bending radius of 7.8 mm)	Yes	30 days
[45]	PSS doped PANI/G	$\Delta R/R_{\text{air}}$	20 (1 ppm) 80 (50 ppm)	1–50	90/150	5 cycles (50 ppm)	Yes	NA
[47]	HCSA doped PANI/PEO	$\Delta R/R_{\text{air}}$	5 (1 ppm) 25 (10 ppm)	1–10	120/250	NA	Yes	45 days
[48]	PANI/Ag	$\Delta I/I_{\text{air}}$	450 (25 ppm)	1–25	300/NA	NA	Yes	NA
[49]	PANI /ZnO	$\Delta R/R_{\text{air}}$	3.2 (0.1 ppm) 53.5 (100 ppm)	0.1–100	63/12	5 cycles (1–30 ppm)	Yes	NA
[50]	$\text{SnO}_2/\text{rGO}/\text{PANI}$	$\Delta R/R_{\text{air}}$	3.18 (0.05 ppm) 91.11 (10 ppm)	0.05–10	80 ~ 82/78 ~ 88	5 cycles (0.1–5 ppm)	Yes	30 days
[51]	Cu^{2+} -doped SnO_2 nanograin/PPy nanosphere	$\Delta I/I_{\text{air}}$	400 (0.05 ppm) 8500 (50 ppm)	0.05–180	7/14	5 cycles (2, 50 ppm)	Yes	32 days
[53]	Cu_xO -polypyrrole aerogels doped with GO	$I_{\text{gas}}/I_{\text{air}}$	1200 (50 ppm)	2–200	~ 20/ ~ 300	NA	Yes	32 days
[54]	PEDOT:PSS/graphene/AgNWs	$R_{\text{air}}/R_{\text{gas}}$	1510 (100 ppm) 14,916,670 (500 ppm)	100–500	NA	NA	NA	30 days

4. Heterojunction engineering

Constructing heterojunctions is crucial for amplifying gas response. Heterojunctions enhance the resistance difference of sensors before and after H₂S exposure, leading to improved sensor sensitivity. A notable example is the p-n junction incorporating CuO. Beyond the inherent enhancement of p-n junctions, CuO reacts with H₂S to form CuS, which converts the p-n junction into a Schottky barrier, further amplifying the response. However, to maintain a reproducible response, the reoxidation of CuS back to CuO must be enhanced through light or heat.

Additionally, we conducted a comprehensive performance analysis of sensors utilizing these enhancement strategies (as shown in Table 1). While these strategies significantly improve sensor response, challenges remain in terms of stability, recovery, and repeatability. With the rapid development of the Internet of Things (IoT) and artificial intelligence (AI), H₂S gas sensors have shown application potential in the fields of health monitoring, food packaging, and environmental surveillance. The concentration of H₂S in exhaled breath is closely associated with gastrointestinal disorders and oral health issues, such as periodontitis and dental caries. Real-time monitoring of H₂S gas content in exhaled gas through wearable devices can help improve physical condition and reduce pain early. H₂S is also a key byproduct of protein decomposition during food spoilage. Monitoring the concentration of H₂S within food packaging in real time allows for dynamic adjustment of storage conditions, thereby extending food shelf life. Moreover, industries such as wastewater treatment, oil and gas, leather manufacturing, and mining generate large amounts of H₂S in exhaust emissions. Real-time detection of environmental H₂S levels is a viable approach to reducing casualties and mitigating environmental pollution. These real-world applications impose stringent requirements on sensors regarding interference resistance, cost-effectiveness, and portability. Future research should focus on developing H₂S gas sensors with low power consumption, high response, superior selectivity, excellent environmental stability, reusability, and compact, portable designs.

Abbreviations

H ₂ S	Hydrogen sulfide
VOC	Volatile organic compounds
CuO	Copper oxide
Fe ₂ O ₃	Iron oxide
SnO ₂	Tin oxide
ZnO	Zinc oxide
MnO ₂	Manganese dioxide
MoO ₃	Molybdenum trioxide
Ti ₃ C ₂ T _x	Titanium carbide
WO ₃	Tungsten trioxide
Bi ₂ WO ₆	Bismuth tungstate
MoS ₂	Molybdenum disulfide
CuS	Copper sulfide

TiO ₂	Titanium dioxide
In ₂ S ₃	Indium sulfide
ZnFe ₂ O ₄	Zinc ferrites
SWCNT	Single-walled carbon nanotube
AgNPs	Silver nanoparticles
G	Graphene
GO	Graphene oxide
rGO	Reduced graphene oxide
PANI	Polyaniline
PPy	Polypyrrole
PEDOT	Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate
HCl	Hydrochloric acid
H ₂ SO ₄	Sulfuric acid
PSS	Poly(4-styrene sulfonic acid)
PAA	Poly(acrylic acid)
PVSA	Polyvinyl sulphonic acid
PAMPSA	Poly(2-acrylamido-2-methyl-1-propanesulfonic acid)
HCSA	Camphor sulfonic acid
PEO	Polyethylene oxide

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Author contributions

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Availability of data and materials

No datasets were generated or analysed during the current study.

Declarations

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

The authors declare no competing interests.

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