



Cite this: *Chem. Commun.*, 2024, 60, 14497

## Recent advances in nanomaterial-enabled chemiresistive hydrogen sensors

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With the growing adoption of hydrogen energy and the rapid advancement of Internet of Things (IoT) technologies, there is an increasing demand for high-performance hydrogen gas (H<sub>2</sub>) sensors. Among various sensor types, chemiresistive H<sub>2</sub> sensors have emerged as particularly promising due to their excellent sensitivity, fast response times, cost-effectiveness, and portability. This review comprehensively examines the recent progress in chemiresistive H<sub>2</sub> sensors, focusing on developments over the past five years in nanostructured materials such as metals, metal oxide semiconductors, and emerging alternatives. This review delves into the underlying sensing mechanisms, highlighting the enhancement strategies that have been employed to improve sensing performance. Finally, current challenges are identified, and future research directions are proposed to address the limitations of existing chemiresistive H<sub>2</sub> sensor technologies. This work provides a critical synthesis of the most recent advancements, offering valuable insights into both current challenges and future directions. Its emphasis on innovative material designs and sensing strategies will significantly contribute to the ongoing development of next-generation H<sub>2</sub> sensors, fostering safer and more efficient energy applications.

Received 14th October 2024,  
Accepted 11th November 2024

DOI: 10.1039/d4cc05430j

rsc.li/chemcomm

### 1. Introduction

With the rapid development of technology, the world is currently faced with a severe energy crisis resulting from excessive exploitation and utilization of non-renewable energy sources. Hydrogen gas (H<sub>2</sub>) has been generally regarded as a crucial component of the global energy system due to its abundance, efficiency, cleanliness and recyclability.<sup>1</sup> In essence, hydrogen energy sources significantly contribute to the sustainable development of our world. However, H<sub>2</sub> has a high burning velocity, a wide flammable range (4–75 vol%), a low ignition energy (0.017 mJ), and a high heat combustion (142 kJ g<sup>-1</sup>), which makes it extremely dangerous during production, transportation, storage, and utilization processes.<sup>2</sup> In addition, its colorless, odorless, and tasteless properties pose challenges for human sensory detection.<sup>3</sup> Therefore, the research and utilization of H<sub>2</sub> sensors are indispensable for achieving real-time and comprehensive detection of H<sub>2</sub>.

In recent years, researchers have been dedicated to the development of H<sub>2</sub> sensors with heightened sensitivity, expanded detection range, accelerated response time, improved stability, enhanced gas

selectivity, and near-room-temperature operability to achieve timely, precise, and convenient H<sub>2</sub> concentration detection. To date, the commercially available H<sub>2</sub> sensors are mainly divided into eight categories based on their fundamental principles and detection methods, including work function, acoustic, optical, catalytic, thermal conductivity, mechanical, electrochemical and resistance types.<sup>2</sup> Among these types, work function based H<sub>2</sub> sensors are micromachinable, small in size, have low cost, and can be mass-produced; however, they are susceptible to drift and exhibit a hysteresis effect.<sup>4</sup> Although acoustic sensors with high sensitivity can operate in the absence of oxygen (O<sub>2</sub>) from room temperature to 100 °C, it is challenging to operate at a higher temperature without interference from humidity and temperature.<sup>2,5</sup> In terms of optical sensors, there is no source of ignition in explosive atmospheres and the utilization of optical fiber transmission makes them immune to electromagnetic interference, but the stringent requirements on the preparation process, complex structure, high cost, and challenging signal monitoring restrict their large-scale industrial application.<sup>6</sup> Catalytic sensors are suitable for the detection of high concentrations of H<sub>2</sub> (>4%) with exceptional stability and prolonged lifespan, but they do possess certain limitations including elevated operational temperatures, increased power consumption, limited capability to differentiate between other combustible gases, and a requirement for 5–10% O<sub>2</sub>.<sup>7</sup> Furthermore, the thermal conductivity sensors have a higher detection limit and a poor selectivity for gases with high thermal conductivity.<sup>2</sup> And the mechanical sensors also have disadvantages including slow response time, susceptibility to

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## Highlight

poisoning and hydrogen-induced aging effects.<sup>2</sup> Compared with the above-mentioned H<sub>2</sub> sensors, both electrochemical and chemiresistive H<sub>2</sub> sensors are considered as state-of-the-art technologies for H<sub>2</sub> sensing nowadays.<sup>8</sup> Nevertheless, the electrochemical sensors are highly susceptible to ambient conditions (temperature, pressure, humidity and oxygen), difficult to integrate, and have rather complicated systems that require high fabrication costs.<sup>9</sup> In contrast, chemiresistive H<sub>2</sub> sensors, which operate by using sensitive materials to react with H<sub>2</sub> and convert chemical reactions into electrical signals (resistance or conductance), have been considered particularly promising for development due to their high sensitivity, fast response, long lifetime, low cost, wide operating temperature range, simple production, and portable applications.<sup>8,10</sup>

There has also been a significant emphasis on chemiresistive H<sub>2</sub> sensors in numerous studies due to the above-mentioned advantages. Generally, the performance of H<sub>2</sub> sensors relies upon the reactions between H<sub>2</sub> and sensing materials. Therefore, accurate processing of the dimensions and shapes of materials is essential for improving sensing performance. With the development of nanotechnology, numerous nanomaterials have been employed for H<sub>2</sub> sensing due to their high surface area-to-volume ratio, abundant surface active sites, high carrier mobility, and interesting physical and chemical properties.<sup>11–15</sup> On the one hand, palladium (Pd) can easily react with H<sub>2</sub> inducing the formation of PdH<sub>x</sub> with a higher resistivity even at room temperature.<sup>16</sup> Thus, Pd-based H<sub>2</sub> sensors have been widely studied owing to their excellent sensing properties, especially their high selectivity and room temperature operation. However, the interference of O<sub>2</sub> molecules in the ambient air significantly hinders the reaction between H<sub>2</sub> and Pd resulting in degraded performance of the sensor in terms of sensitivity and response speed,<sup>17</sup> while the sluggish diffusion of H atoms in Pd lattices also leads to severe hysteresis of the sensor.<sup>18</sup> These challenges present obstacles to the advancement of high-performance H<sub>2</sub> sensor technology. Therefore, researchers are currently focusing on enhancing the sensing characteristics of Pd-based H<sub>2</sub> sensors by investigating various aspects such as Pd nanostructures, Pd-based bimetals, and Pd-based composites. On the other hand, metal oxide semiconductor (MOS)-based sensors, which rely on the modulation of electrical signals resulting from the interaction between H<sub>2</sub> and chemisorbed oxygen on the surface of MOSSs, have also been extensively employed for H<sub>2</sub> sensing in diverse applications. Nevertheless, the adsorption and desorption of O<sub>2</sub> of MOS-based sensors typically require elevated temperatures exceeding 200 °C,<sup>19</sup> thereby restricting their commercial application due to the increased power consumption and reducing their selectivity owing to the high reactivity of other interfering gases induced by elevated temperatures. Consequently, to tackle these challenges, researchers have devised diverse effective approaches, encompassing the design of nanostructures, functionalization by noble metals, doping of elements, and constructing heterojunctions. Besides, emerging materials also demonstrate remarkable H<sub>2</sub> sensing capabilities at room temperature, such as graphene, carbon nanotubes (CNTs), transition metal disulfides (TMDs), and MXenes. Thus, owing to technological advancements, the scope of research on hydrogen-sensitive materials is continuously broadening.

In this review, we classify chemiresistive H<sub>2</sub> sensors into three categories from the perspective of sensitive materials: metal-based, MOS-based, and other materials (graphene, CNTs, TMDs, and MXenes). Firstly, we present a detailed introduction to the gas-sensing mechanisms employed by each type of chemiresistive H<sub>2</sub> sensor. Subsequently, we provide a comprehensive overview of the latest research progress and development strategies for high-performance chemiresistive H<sub>2</sub> sensors, focusing primarily on elucidating the physicochemical mechanisms that contribute to enhanced sensing performance through various improvement methods. We particularly emphasize the intricate relationship between sensing performance and factors such as structural characteristics, surface modifications, and chemical and electrical properties. Finally, we conclude the status of H<sub>2</sub> sensor research, point out existing limitations, and provide prospects for future research directions.

## 2. Metal-based H<sub>2</sub> sensors

Among various metals for H<sub>2</sub> sensors, Pd has been known as the most appealing material due to its unique ability to reversibly and selectively form PdH<sub>x</sub> in the presence of H<sub>2</sub> under ambient conditions at room temperature. Therefore, there have been developed numerous Pd-based H<sub>2</sub> sensors, including Pd nanostructures, Pd-based bimetals and Pd-based composites. Additionally, except for Pd, Pt also exhibits a gas response to H<sub>2</sub>. O<sub>2</sub> molecules in the surrounding air are readily dissociated and adsorbed onto the surface of Pt, leading to an increase in Pt resistance due to electron scattering on the adsorbed oxygen molecules. Subsequently, upon exposure to H<sub>2</sub>, the catalytic conversion of adsorbed oxygen into water occurs while H<sub>2</sub> chemisorbs onto the surface of Pt forming Pt–H, resulting in a decrease in resistance unlike Pd.<sup>8,20</sup> The response time of Pt towards H<sub>2</sub> exposure was observed to be faster compared to that of Pd under the same operating conditions.<sup>20</sup> However, a significant limitation of Pt-based sensors is that they exhibit identical resistance change for H<sub>2</sub> concentrations exceeding 0.1% due to early saturation, which greatly limits their practical applications.<sup>20,21</sup> Consequently, limited subsequent research has been conducted on pure Pt-based sensors. In this section, we provide a detailed discussion on sensing mechanisms and recent advancements related to Pd-based H<sub>2</sub> sensors.

### 2.1. Sensing mechanisms for Pd-based H<sub>2</sub> sensors

In general, the sensing mechanisms of Pd-based H<sub>2</sub> sensors are attributed to the formation of PdH<sub>x</sub>. H<sub>2</sub> molecules are easily adsorbed on the surface of Pd and dissociated into H atoms at room temperature (eqn (1) and (2)). Then, the H atoms spontaneously and selectively diffuse into the octahedral interstitial sites of the face-centered cubic (FCC) Pd lattice (Fig. 1a).<sup>22</sup> In the Pd–H system, PdH<sub>x</sub> usually has two phases ( $\alpha$  phase and  $\beta$  phase) due to the different H<sub>2</sub> pressures.<sup>1</sup> When exposed to an H<sub>2</sub> pressure below 1%, Pd undergoes partial filling of its interstitial sites, leading to the formation of a solid-solution phase ( $\alpha$  phase, eqn (3)).<sup>22</sup> With the increase of H<sub>2</sub> pressure (1% < [H<sub>2</sub>] < 2%), the interaction between dissolved H atoms in Pd metal becomes more

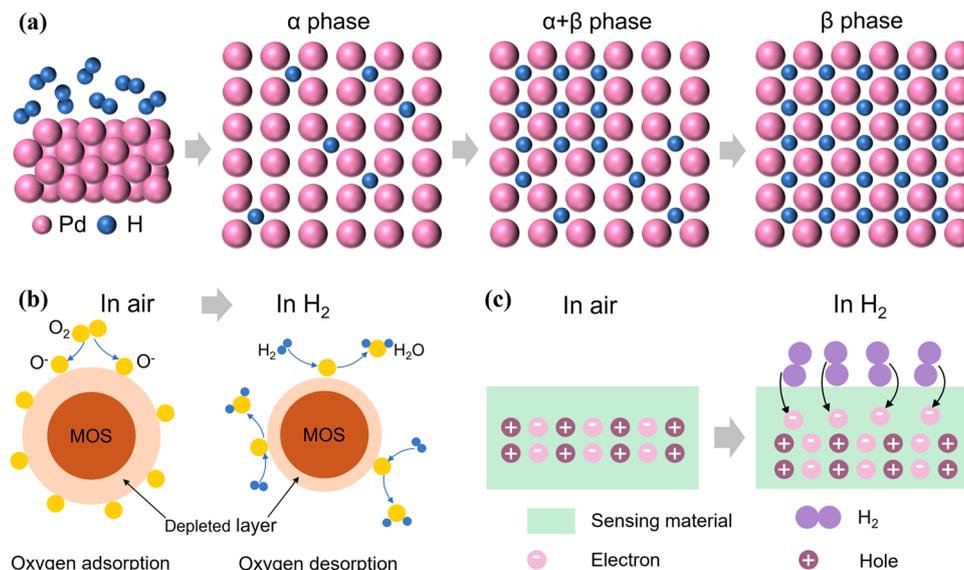
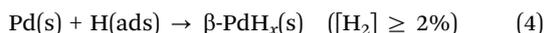
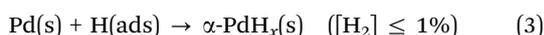
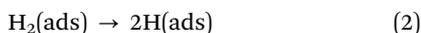
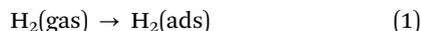


Fig. 1 (a) Schematic of hydrogen diffuse into the Pd lattice. (b) Schematic of chemisorption based on MOSs. (c) Schematic of physisorption.

pronounced, which induces the first transition in the  $PdH_x$  matrix.<sup>23,24</sup> Simultaneously, nucleation of the  $\beta$  phase occurs within the  $\alpha$  phase and subsequently the  $\alpha$  and  $\beta$  phases coexist until a complete phase transition from  $\alpha$  to  $\beta$  ( $[H_2] \geq 2\%$ , eqn (4)).<sup>24</sup> Moreover, both  $\alpha$ - $PdH_x$  and  $\beta$ - $PdH_x$  exhibit a higher resistivity compared to Pd, because the H atoms occupied in the interstitial sites act as scattering sites impeding the movement of free electrons.<sup>8</sup> Generally, the increase in resistivity resulting from the formation of  $PdH_x$  is considered the primary sensing mechanism for most of the Pd-based  $H_2$  sensors. However, the further formation of  $\beta$  phase induces significant volume expansions in the Pd lattice, which results in irreversible structural changes in Pd. Consequently, achieving linear detection of high concentrations of  $H_2$  ( $[H_2] \geq 2\%$ ) while maintaining excellent long-term stability poses a formidable challenge. Additionally, the presence of interfering gases, which is inevitable in practical applications, will influence the permeability of  $H_2$ . The carbon monoxide (CO), nitrogen oxides, or hydrocarbon instead of  $H_2$  competitively adsorb on the site of Pd and occupy the active sites, thereby reducing the  $H_2$  permeability into the Pd and further reducing the selectivity.<sup>25–27</sup> Therefore, in practical applications, it is also necessary to consider how to eliminate the influence of interfering gases.



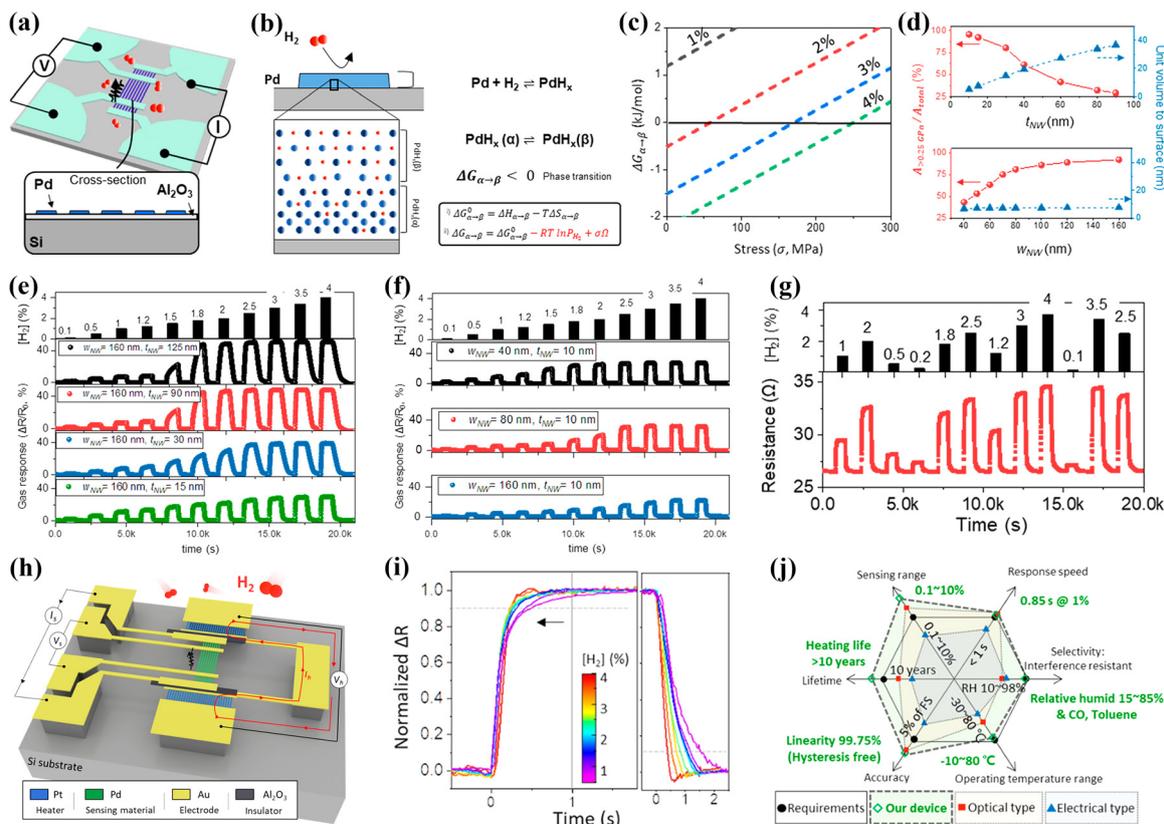
## 2.2. Pd nanostructures

With the development of nanomaterials and nanotechnology, numerous Pd nanostructures, including Pd nanoparticles (NPs),<sup>28</sup> Pd nanowires (NWs),<sup>29–31</sup> Pd nanosheets,<sup>32</sup> and Pd nano hollow shells,<sup>33</sup> have been explored for  $H_2$  sensors. Pd

nanostructures have significant advantages for  $H_2$  sensing applications due to their high surface area-to-volume ratio, electron transport ability, high porosity, and exposure of high-energy facets that are catalytically active.<sup>31</sup>

Among them, Pd NWs have been the most extensively studied. It was previously reported that precise control and design of the size of Pd NWs are critical for achieving highly efficient  $H_2$  sensing.<sup>34</sup> However, conventional lithography techniques are incapable of fabricating Pd NWs with a diameter smaller than 10 nm and also entail relatively high costs. Solution-phase synthesis enables the production of Pd NWs exhibiting an exceptionally high aspect ratio and small diameter, but they are typically capped with surfactants or ligands that pose challenges in their removal and interfere with sensing applications.<sup>35</sup> As a consequence, to address the aforementioned limitations, Kumar *et al.*<sup>31</sup> showed a solution-phase synthesis of Pd NWs with an ultrathin diameter smaller than 5 nm and treated with an ultraviolet (UV-O) source to remove the ligands attached to their surface. Subsequently, a comparative analysis was conducted to evaluate the  $H_2$  sensing performance pre and post UV-O treatment, revealing that the sensor subjected to UV-O treatment exhibited enhanced sensitivity along with accelerated response and recovery speed. Additionally, the UV-O-treated sensor displayed response and recovery time of 3.4 and 11 s to 1%  $H_2$  with high selectivity to  $H_2$  in comparison with CO,  $CO_2$ , and  $CH_4$ . After being exposed to 100 ppm CO for 2 minutes, which was much higher than the allowable concentration in the ambient environment, the response to 100 ppm  $H_2$  only decreased by 10%. However, the author only mentioned short-term repeatability within 30 minutes, neglecting to investigate the long-term stability, which was one of the primary concerns in practical applications. In general, the high properties of the Pd NW-based sensor can be ascribed to its ligand-free surface and ultrathin diameter.

Interestingly, Jo *et al.*<sup>29</sup> developed a phase-transition-inhibited Pd NW sensor with a linear response at 4%  $H_2$ . The



**Fig. 2** (a) Schematic illustration of the Pd NW H<sub>2</sub> sensor. (b) Schematic of the internal lattice structure of Pd NWs with two phases and the thermodynamic quantities related to H<sub>2</sub> pressure and stress for the phase transition of PdH<sub>x</sub> from  $\alpha$  to  $\beta$ . (c) Gibbs free energy of the PdH<sub>x</sub> phase transition varied with stress ( $\sigma$ ) at four different concentrations of H<sub>2</sub>. (d) Curves of  $A_{>0.25\text{ GPa}}/A_{\text{total}}$  and unit volume to surface concerning  $t_{\text{NW}}$  or  $w_{\text{NW}}$ . (e) Response–recovery curves of Pd NW sensors with different  $t_{\text{NW}}$  and fixed  $w_{\text{NW}}$  (160 nm) to different H<sub>2</sub> concentrations ranging from 0.1 to 4%. (f) Response–recovery curves of Pd NW sensors with different  $w_{\text{NW}}$  and fixed  $t_{\text{NW}}$  (10 nm) to different H<sub>2</sub> concentrations ranging from 0.1 to 4%. (g) Response–recovery curves of Pd NW sensors to various random H<sub>2</sub> concentrations ( $w_{\text{NW}} = 160\text{ nm}$ ,  $t_{\text{NW}} = 15\text{ nm}$ ). Reproduced with permission from ref. 29. Copyright 2022 American Chemical Society. (h) Schematic representation of the Pd nanoelectromechanical H<sub>2</sub> sensing device and its structural characteristics for rapid H<sub>2</sub> detection. (i) Response/recovery time for Pd NW sensors of different H<sub>2</sub> concentrations from 1–4%. (j) Chart of the six required performances in H<sub>2</sub> detection compared the four different types of devices. Reproduced with permission from ref. 30. Copyright 2023 American Chemical Society.

H<sub>2</sub> sensing device, as illustrated in Fig. 2a, comprised a precisely aligned array of Pd NWs serving as the sensing material along with four electrodes. Since the bottom of Pd NWs was fixed to the substrate, compressive stress was generated near the substrate to partially inhibit volume expansion when H diffused into the interstitial sites of Pd. The inhibition of the PdH<sub>x</sub> phase transition in the high-stress region can be explained by the change of the free energy equation (Fig. 2b). According to ideal solid solution absorption effects, free energy was directly influenced by H<sub>2</sub> pressure ( $P_{\text{H}_2}$ ) and internal stress of the solid. The internal stress restricted the diffusion of atoms within the solid, leading to a change in chemical potential and an enhancement of  $\alpha$ -phase PdH<sub>x</sub> stability. Consequently, when sufficiently high stress was generated in Pd NWs, diffusion of H atoms became challenging, thereby achieving an inhibitory effect on phase transition. Furthermore, it was determined that a critical stress of at least 0.25 GPa was required in PdH<sub>x</sub> to successfully inhibit the phase transition at 4% H<sub>2</sub> (Fig. 2c) and it was presumed that regions with a high  $A_{>0.25\text{ GPa}}/A_{\text{total}}$ , especially above 90%, are imperative for effectively inhibiting

phase transition due to variations in stress induced by the size of the Pd NWs. As shown in Fig. 2d, the Pd NWs with width ( $w_{\text{NW}}$ ) greater than 160 nm and thickness ( $t_{\text{NW}}$ ) less than 15 nm were suitable for phase transition inhibition and fast response time. To verify the theoretical predictions experimentally, they compared the H<sub>2</sub> response of Pd NWs with different widths and thicknesses. The Pd NWs with a width of 160 nm and a thickness exceeding 15 nm exhibited an abrupt increase in sensitivity at 1.5% of H<sub>2</sub>, indicating the initiation of  $\beta$ -phase transition and then showed identical gas responses from 2 to 4% of H<sub>2</sub> because of the saturation of H content in the nanowire (Fig. 2e). Moreover, a similar phenomenon was also displayed in Pd NWs with a thickness of 10 nm and a width below 160 nm (Fig. 2f). Therefore, the Pd NWs with a width of 160 nm and a thickness of 10 nm exhibited linear response and repeatable performance to H<sub>2</sub> concentrations from 0.1 to 4% (Fig. 2f and g).

It has already been above-mentioned that the phase transition is accompanied by an increase in resistance; however, as the H<sub>2</sub> concentration further increases, it is difficult to

distinguish the concentration of H<sub>2</sub> due to the saturation of H<sub>2</sub> resulting in the saturation of resistance. Therefore, it becomes challenging to achieve linear detection up to 10% H<sub>2</sub>. Meanwhile, the application of thermal energy to activate Pd has been recognized as an efficacious approach to accelerate the response rate without material engineering by improving the H<sub>2</sub> adsorption efficiency and impeding the phase transition of PdH<sub>x</sub>.<sup>36</sup> Accordingly, the following year, Jo *et al.*<sup>30</sup> designed a coplanar Pt NW heater-integrated sensing architecture for optimal thermal activation of pure Pd NWs to achieve a subsecond (~0.6 s) response time and a linear detection of up to 10% H<sub>2</sub>. The structure of the device can maximally expose the reaction sites of Pd NWs and form a uniform temperature in the sensing elements by constructing a conductive heat transfer design (Fig. 2h). Therefore, this sensor displayed a fast response time of 0.6 s in the concentration range of 1–4%, a wide detection range of 0.1–10% with 99.75% linearity and durable heating operation in a wide temperature range (–10 to 80 °C) with high repeatability (>104 cycles) and a long heating lifetime (>10 years) (Fig. 2i and j). It's worth noting that the influence of CO and high humidity can be ignored due to the high operating temperature, which lowered the adsorption of CO and condensation of water. However, the detection of high concentrations of H<sub>2</sub> is always accompanied by a poor long-term stability, which was not investigated in this paper. On the whole, the synergistic effect of nanostructures and thermal activation can significantly enhance the H<sub>2</sub> sensing characteristics.

### 2.3. Pd-based bimetals

To mitigate the irreversible damage caused by the  $\alpha$ - $\beta$  phase transition of PdH<sub>x</sub> in Pd-based H<sub>2</sub> sensors, it is common practice to employ Pd-based bimetals as hydrogen-sensitive materials instead of pure Pd. This strategy has been shown to effectively mitigate phase changes by occupying Pd's interstitial sites with different metal atoms.<sup>29</sup> Furthermore, the Pd-based bimetals have superior activity for surface reactions relative to pure Pd. Commonly, the metal elements used to form bimetals with Pd are Pt, Au, Ag, Sn and Ni.<sup>37–44</sup>

Owing to the same FCC structure and minimal lattice mismatch (0.77%),<sup>45</sup> Pt is a promising candidate for the synthesis of Pd-based bimetals. One recent advance in Pd-based bimetals was the demonstration of a facile synthesis of ultra-small bimetallic nanoparticles (BM-NPs) of PdPt produced within porous ion-exchange polymers to create high-performance H<sub>2</sub> sensors that enable wireless detection reported by Koo *et al.* (Fig. 3a).<sup>40</sup> Herein, the porous ion-exchange polymer of imidazolium-functionalized triptycene polyether sulfone (ITPES) enabled homogeneous diffusion and immobilization of an ionic metal precursor of complementary charge into the polymer matrix, thus achieving precise regulation of the size (down to 1 nm) and composition of BM-NPs, which was critically important for sensing performance. Furthermore, upon exposure to H<sub>2</sub>, due to the synergistic effect of PdPt NPs, two reactions occurred: (1) the removal of surface-adsorbed oxygen resulted in a decrease in resistance, and (2) H<sub>2</sub> adsorption led to an elevation in resistance (Fig. 3b). The two reactions occurred

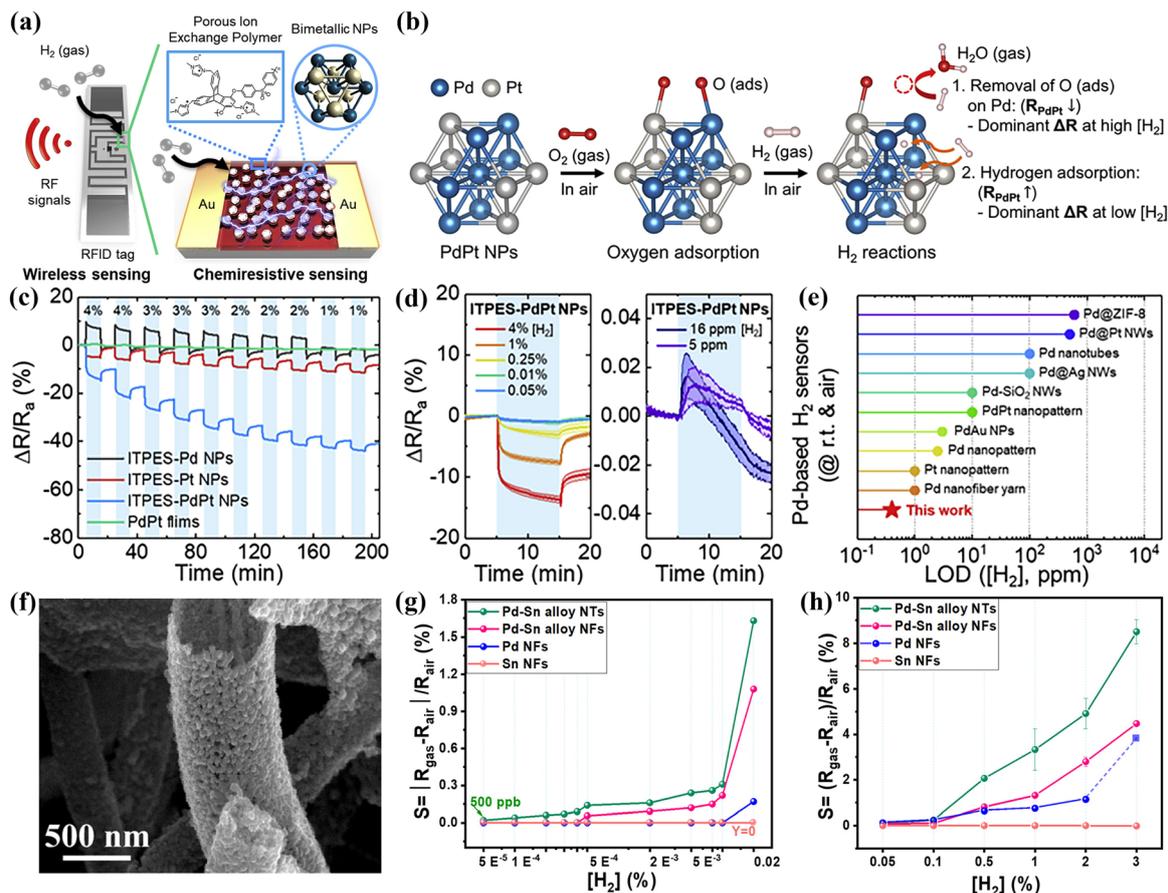
simultaneously, with the former dominating the resistance at high levels of [H<sub>2</sub>], while the latter prevailed at low levels of [H<sub>2</sub>]. Thus, the resistance of the ITPES-PdPt NPs sensors decreased when exposed to H<sub>2</sub> concentrations above 100 ppm and then switched to an increase in resistance with H<sub>2</sub> exposures below 16 ppm (Fig. 3d). Based on these results, the ITPES-PdPt NP-based sensor demonstrated remarkable stability and excellent H<sub>2</sub> sensing properties with a response of 15.7% to 4% H<sub>2</sub> and a low detection limit of 0.4 ppm (Fig. 3c–e). However, a linear gas response had not been achieved. Therefore, the reliability of the sensor necessitated further enhancement. In general, it is imperative to enhance the H<sub>2</sub> sensing performance through the synthesis of small-sized (below a few nanometers) Pd-based bimetallic NPs exhibiting exceptional surface activity.

In addition, various Pd-based bimetals can improve H<sub>2</sub> sensing performances by constructing nanostructures with high specific surface area and multiple active sites. In this regard, Song *et al.*<sup>43</sup> firstly fabricated hollow Pd–Sn alloy nanotubes (NTs) with a high surface area and ultrafine grain sizes by relying on particle migration and coalescence of neighboring particles. As shown in Fig. 3f, the SEM image revealed the shape of the Pd–Sn NTs in a hollow morphology having high porosity with superfine grain sizes. Besides, compared to Pd–Sn alloy nanofilms (NFs), Pd NFs and Sn NFs, the Pd–Sn NTs exhibited excellent sensitivity toward H<sub>2</sub> (0.00005–3%) and a high response of 9.27% to a concentration of H<sub>2</sub> (3%) at room temperature due to the highly porous structure with smaller nanograins offering more exposed active sites and higher gas accessibility (Fig. 3g and h). From the results, it is an efficient method to develop Pd-based bimetals with special nanostructures for the improvement of the H<sub>2</sub> sensing performance.

However, the above-mentioned sensors exhibit long response/recovery times, which limits their application. Usually, appropriately increasing the operating temperature of the sensor will accelerate the diffusion of H<sub>2</sub> resulting in a faster response/recovery speed. For instance, Liu *et al.*<sup>41</sup> proposed a heating operation mode of the Pd/Ni-based H<sub>2</sub> sensor integrating with a Pt heating wire. They found that the Pd/Ni film demonstrated a short response/recovery time of 7/6 s to 2% H<sub>2</sub> at the optimal temperature of 75 °C. In addition, Deepti *et al.*<sup>37</sup> reported that Pd–Au alloy exhibited a significantly reduced response/recovery time (7/50 s) to 2% H<sub>2</sub> at 250 °C due to the ion irradiation, whereas the pristine sample displayed long response/recovery time (114/78 s). This improvement can be attributed to the ion-irradiation induced defects, which enhance the rate of H<sub>2</sub> absorption. Nevertheless, the elevated operating temperature of 250 °C is accompanied by high power consumption, thereby impeding their commercial applications. Therefore, further investigation is imperative to facilitate the attainment of rapid response and recovery capabilities for this type of sensor while operating at near room temperature.

### 2.4. Pd-based composites

The combination of Pd with other materials induces synergistic effects, thus improving stability, enhancing sensitivity, and accelerating the response/recovery speed of the Pd-based



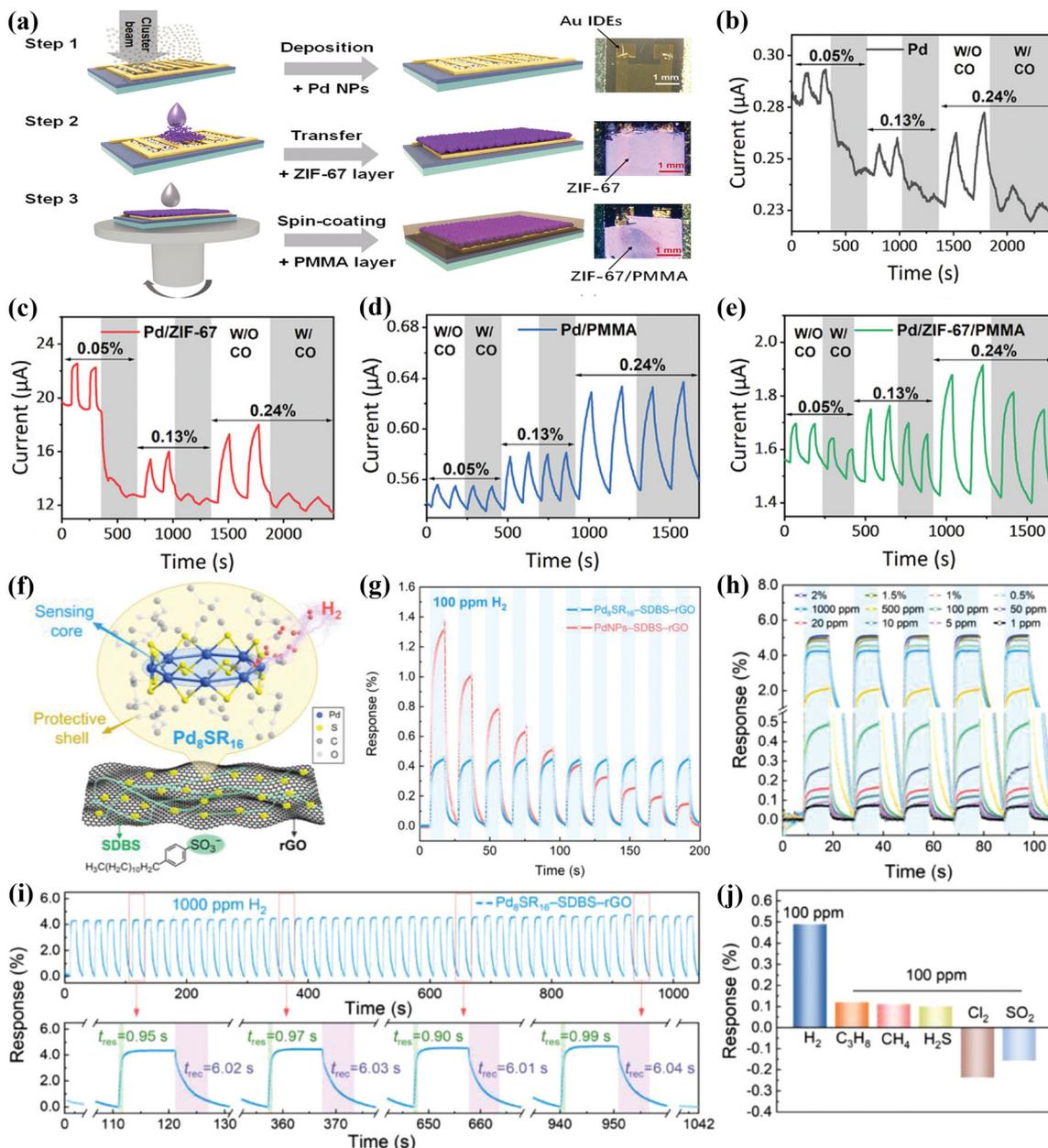
**Fig. 3** (a) Schematic illustration of the chemiresistive H<sub>2</sub> sensing system with wireless detection. (b) Schematic illustration of the H<sub>2</sub> sensing mechanisms of ITPES-PdPt NPs. (c) Response–recovery curves of ITPES-Pd NPs, ITPES-Pt NPs, ITPES-PdPt NPs, and PdPt films at room temperature to different H<sub>2</sub> concentrations ranging from 1 to 4%. (d) Response–recovery curve of ITPES-PdPt NPs to 5 and 16 ppm and 0.05%, 0.01%, 0.25%, 1%, and 4% of H<sub>2</sub> at room temperature. (e) Comparison of the detection limits of different Pd-based H<sub>2</sub> sensors. Reproduced with permission from ref. 40. Copyright 2020 Elsevier. (f) Schematic illustration of the synthesis process for Pd–Sn alloy NTs. (g) Normalized response ( $S$ ) versus H<sub>2</sub> concentrations for Pd–Sn alloy NTs, Pd–Sn alloy NFs, Pd NFs, and Sn NFs at H<sub>2</sub> concentrations of 0.5–200 ppm and (h) 5000–3000 ppm. Reproduced with permission from ref. 43. Copyright 2022 American Chemical Society.

sensors by using Pd-based composites. To date, many Pd-based composites have been developed, effectively addressing numerous challenges encountered in practical applications.<sup>46–51</sup>

For instance, Xing *et al.*<sup>50</sup> developed an H<sub>2</sub> sensor by using Pd NPs decorated on the carbon/nitrogen porous framework. It exhibited a wide concentration range of 200 ppm to 40% ( $S \approx 73.8\%$  and  $T_{res} \approx 9$  s) H<sub>2</sub> sensing at room temperature, showing exceptional long-term stability with reliable H<sub>2</sub> sensing maintained for up to 142 days. The exceptional performance can be attributed to the presence of Mott–Schottky heterojunctions between Pd NPs and N-doped carbon materials and the three-dimensional (3D) porous structures, which show excellent catalytic activity and provide abundant surface sites for gas diffusion and adsorption due to their large specific surface area. This result demonstrates the efficacy of incorporating other materials with Pd to enhance stability and reduce response/recovery time, thereby offering an efficient approach for improving Pd-based H<sub>2</sub> sensors.

However, Pd-based H<sub>2</sub> sensors are susceptible to poisoning and deactivation due to the adsorption of CO, nitrogen oxides,

or hydrocarbons.<sup>27,52</sup> Due to the relatively smaller size of H<sub>2</sub> compared to other molecules, applying a polymer coating on H<sub>2</sub> sensing materials can effectively act as a molecular sieve. However, this approach usually results in an extended response time and a compromised sensitivity of the sensor. Therefore, to overcome these issues, Xie *et al.*<sup>49</sup> constructed a triple-layer Pd nanocluster film-metal organic framework (MOF)-polymer hybrid nanocomposite for H<sub>2</sub> detection. Among them, the polymethyl methacrylate (PMMA) membrane acted as a molecular sieve, while the zeolitic imidazole framework-67 (ZIF-67) film served as an interfacial layer between the Pd NC film and the protective PMMA layer (Fig. 4a). To confirm that this structure had a good ability to resist CO poisoning without causing degradation of the sensor performance, they conducted an H<sub>2</sub> sensing test in a CO background for various sensor types, including Pd, Pd/ZIF-67, Pd/PMMA, and Pd/ZIF-67/PMMA. As shown in Fig. 4b and c, the presence of ZIF-67 film greatly enhanced the sensitivity of the sensor; however, upon exposure to CO, their performances were significantly diminished. However, even in the presence of CO, both Pd/PMMA and



**Fig. 4** (a) Schematic illustration of the fabricated Pd/ZIF-67/PMMA sensor. Response–recovery curves of (b) Pd, (c) Pd/ZIF-67, (d) Pd/PMMA, and (e) Pd/ZIF-67/PMMA to H<sub>2</sub> with different concentrations along with 1% CO gas. Reproduced with permission from ref. 49. Copyright 2022 Wiley-VCH GmbH. (f) Structure diagram for Pd<sub>9</sub>SR<sub>16</sub>-SDBS-rGO used for H<sub>2</sub> sensing. (g) Response–recovery curves for Pd<sub>9</sub>SR<sub>16</sub>-SDBS-rGO and PdNPs-SDBS-rGO sensors to 100 ppm H<sub>2</sub> at room temperature. (h) Response–recovery curve of the Pd<sub>9</sub>SR<sub>16</sub>-SDBS-rGO sensor to different H<sub>2</sub> concentrations ranging from 1 ppm to 2%. (i) 50-cycle response–recovery curve and response/recovery time for the Pd<sub>9</sub>SR<sub>16</sub>-SDBS-rGO sensor to 1000 ppm H<sub>2</sub> at room temperature. (j) Selectivity of Pd<sub>9</sub>SR<sub>16</sub>-SDBS-rGO towards H<sub>2</sub> in comparison with interfering gases including C<sub>3</sub>H<sub>8</sub>, CH<sub>4</sub>, H<sub>2</sub>S, Cl<sub>2</sub>, and SO<sub>2</sub>. Reproduced with permission from ref. 46. Copyright 2024 Wiley-VCH GmbH.

Pd/ZIF-67/PMMA exhibited consistent responses upon the introduction of the PMMA membrane (Fig. 4d and e). Hence, these results indicated that the obtained Pd/ZIF-67/PMMA hydride nanostructure effectively mitigated performance degradation associated with a single polymer coating and synergistically combined the satisfactory CO-poisoning resistance conferred by the PMMA membrane with improved sensing performance provided by the ZIF-67 film. In conclusion, Pd/

ZIF-67/PMMA demonstrated optimal comprehensive performance owing to its unique nanocomposite structure.

In addition to the formation of bimetals, Pd nanoclusters (NCs) also exhibit the ability to impede phase transitions through diverse H<sub>2</sub> binding mechanisms.<sup>46,53</sup> Moreover, metal NCs display atomic precision in composition, exceptional efficiency in metal utilization, and highly controllable geometries; thus, they emerge as promising candidates for sensing

Table 1 Summary of the sensing properties of Pd-based H<sub>2</sub> sensors

Material	Morphology	Conc. (%)	Tem. (°C)	Res. (%)	$T_{res}/T_{rec}$ (s)	MDL (ppm)	Ref.
Pd	Hollow shells	1	RT	60	16/—	75	33
Pd	Nanoparticles	1	RT	30.65	11.6/15.7	—	31
Pd	Nanowires	1	RT	1.7	3.4/101	10	31
Pd	Nanowires	4	RT	35.9	21/270	1000	29
Pd	Nanosheets	1	RT	0.4	50/60	5	51
Pd	Nanowires	1	RT	0.34	12/28	200	35
Pd–Sn	Nanotubes	2	RT	4.8	20.2/17.9	1	43
PdPt	Nanoparticles	1	RT	7.56	92/304	0.4	40
Pd/Ni	Film	2	75	3.17	7/6	4000	41
Pd–Au	Film	2	250	9.1	7/50	—	37
MWCNT@Pd	Nanosheets	1	RT	3.6	74/25	5	51
Pd@rGO	Nanowires	1	RT	2.06	52/45	20	35
Pd@rGO@ZIF-8	Nanowires	1	RT	2.17	5/31	20	35
Pd <sub>8</sub> SR <sub>16</sub> –SDBS–rGO	Nanoclusters	0.1	RT	4	0.9/6	1	46
Pd–rGO	Nanoparticles	2	RT	14.8	73/126	25	48

Conc.: gas concentration; Tem.: operating temperature of the sensor; Res.: response of the sensor and response is defined as  $(R_{gas} - R_{air})/R_{air} \times 100\%$ ;  $T_{res}$ : response time of the sensor;  $T_{rec}$ : recovery time of the sensor; MDL: minimum detection limit of the sensor; Ref.: reference; -: not reported; RT: room temperature ( $\sim 25$  °C); MWCNT: multiwalled carbon nanotube.

applications.<sup>54</sup> However, attaining stable existence for pure metal nanoclusters has proven to be a formidable challenge due to their elevated surface energy and reactivity.<sup>55</sup> Recently, a new advance of the Pd NC-based composites in H<sub>2</sub> sensing was reported by Chen *et al.*<sup>46</sup> They introduced thiolate-protected Pd nanoclusters (Pd<sub>8</sub>SR<sub>16</sub>), which unveiled the first-time application in H<sub>2</sub> sensing, showing the significant potential for rapid detection. Amongst others, the synergistic interaction between metal and ligand of Pd<sub>8</sub>SR<sub>16</sub> resulted in the formation of an intermediate palladium–hydrogen–sulfur (Pd–H–S) state during H<sub>2</sub> adsorption. This state preserved the Pd–H binding while preventing excessive interaction, achieving a balance that reduced the activation energy required for H<sub>2</sub> desorption and facilitating highly reversible and rapid response/recovery. Furthermore, the Pd<sub>8</sub>SR<sub>16</sub> as H<sub>2</sub> sensing sites were deposited on a sodium dodecylbenzene sulfonate/reduced graphene oxide (SDBS–rGO) carrier layer. The resulting Pd<sub>8</sub>SR<sub>16</sub>–SDBS–rGO sensor (Fig. 4f) effectively mitigated the restrictions associated with conventional Pd-based sensors across varying H<sub>2</sub> concentrations, including durability degradation or failure arising from excessive Pd–H binding or phase transitions. As shown in Fig. 4g, compared to the PdNPs–SDBS–rGO sensor, the Pd<sub>8</sub>SR<sub>16</sub>–SDBS–rGO sensor exhibited consistent signal stability across 10 cycles at a low H<sub>2</sub> concentration of 100 ppm, owing to the protection of thiolate. Additionally, the Pd<sub>8</sub>SR<sub>16</sub>–SDBS–rGO sensor displayed a wide detection range of H<sub>2</sub> concentrations from 1 ppm to 2% (Fig. 4h) and showed a stable and prompt response ( $t_{res} = 0.95$  s) and recovery ( $t_{rec} = 6$  s) at 1000 ppm H<sub>2</sub> (Fig. 4i). The practical application of this sensor effectively mitigated the interference from other gases due to the superior selectivity (Fig. 4j). Therefore, this study demonstrated the practicality of using ligand-protected metal nanoclusters for gas sensing in the real-world. From this perspective, researchers can employ diverse materials in conjunction with Pd to fulfill the practical application demands of H<sub>2</sub> sensing.

Currently, significant advancements have been achieved in the research on Pd-based H<sub>2</sub> sensors. The suppression of the

phase transition can be effectively achieved through the design of devices and construction of bimetals, while the selectivity of the sensor has been enhanced through the incorporation of polymer coatings. Table 1 summarizes the sensing performance of Pd-based sensors in recent years. These sensors all exhibit high H<sub>2</sub> sensing performances, in terms of sensitivity, response/recovery speed, and detection limit. However, to mitigate the risk of H<sub>2</sub> explosions, it is imperative to reduce the response/recovery time for concentrations exceeding 1% H<sub>2</sub> to below 1 s. Therefore, further investigation is warranted to develop Pd-based H<sub>2</sub> sensors with faster response/recovery speed.

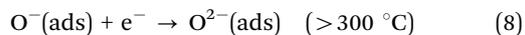
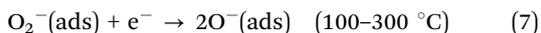
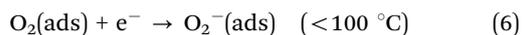
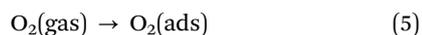
### 3. MOS-based H<sub>2</sub> sensors

The MOS-based resistive gas sensors have attracted considerable attention owing to their remarkable stability, high sensitivity, rapid response/recovery time, low cost, and simple manufacturing process,<sup>10,56,57</sup> rendering them a primary research focus for H<sub>2</sub> sensors. However, the gas sensitivity of MOS-based sensors relies on the redox reaction with adsorbed oxygen, enabling electron exchange with a diverse range of gases and inherently limiting gas selectivity. Simultaneously, in order to ensure enough carriers entering the conduction band for active participation in the reaction, a substantial number of MOS-based gas sensors necessitate elevated operating temperatures exceeding 200 °C.<sup>10,19</sup> The elevated operating temperature not only increases power consumption, impacts device integration, and compromises the gas selectivity of the sensor but also provides an additional ignition source, thereby posing safety hazards in proximity to combustible gases. Moreover, prolonged exposure to elevated temperatures can have a detrimental impact on the long-term stability of sensors by attenuating their sensitivity. Thus, in recent years, extensive research efforts have aimed at enhancing the gas selectivity and reducing the operational temperature of MOS-based H<sub>2</sub> sensors. In this section, we elucidate the fundamental sensing mechanisms and present

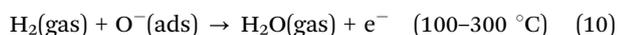
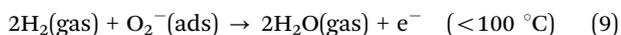
recent advancements in the development of MOS-based H<sub>2</sub> sensors, focusing on MOS nanostructures, modification of noble metal NPs, doping of elements, and MOS-based composites.

### 3.1. Sensing mechanisms for MOS-based H<sub>2</sub> sensors

In general, the mechanism of MOS-based H<sub>2</sub> sensors is a change of electrical signals (current or resistance) caused by the interaction between H<sub>2</sub> and chemisorbed oxygen on the surface of MOSs. The reception of H<sub>2</sub> signals in the air background by MOSs primarily relies on two reactions that occur on the surface of MOSs: O<sub>2</sub> adsorption leading to the formation of reactive oxygen species, and subsequent reaction between these reactive oxygen species and H<sub>2</sub> (Fig. 1b). The O<sub>2</sub> in the air readily absorbs onto the surface of the sensing materials, acting as an acceptor of electrons and dissociating on the surface of MOSs to capture electrons from the conduction band, resulting in the formation of species such as O<sub>2</sub><sup>-</sup>, O<sup>-</sup>, and O<sup>2-</sup>. The adsorption reaction of oxygen is temperature-dependent (eqn (5)–(8)).<sup>58,59</sup>



MOSs can be classified as either n-type or p-type, depending on whether the dominant carriers are electrons or holes. In the case of n-type MOSs, the adsorbed oxygen on the surface of the MOSs acts as a defect site and induces the Fermi level pinning effect. This effect leads to a reduction in electron density on the surface of MOSs, thereby forming an electron depletion layer (EDL) around the MOSs with a high potential barrier. The resistances of MOSs are significantly increased by the EDL, which arises from the reduction in net carrier density and the formation of potential barriers at the adsorption sites.<sup>8,11</sup> When MOSs are exposed to H<sub>2</sub>, a reducing gas, H<sub>2</sub> reacts with the adsorbed oxygen to generate water and release free electrons (eqn (9) and (10)).<sup>60</sup> Consequently, the thickness of the EDL decreases, accompanying the decrease of the resistance of the MOS hydrogen gas sensors.<sup>61</sup> Upon re-exposure to atmospheric conditions, chemisorbed oxygen is formed as O<sub>2</sub> from the air gets adsorbed onto the surface of n-type MOSs again, increasing in resistance.



On the other hand, p-type MOSs exhibit an opposite behavior to n-type MOSs. The combination of adsorbed oxygen and electrons will generate additional holes on the surface of the p-type MOSs, thereby forming a hole accumulation layer (HAL). However, the reaction of H<sub>2</sub> with adsorbed oxygen effectively neutralizes these holes by releasing electrons, leading to a reduction in the thickness of the HAL and an increase in resistance. Subsequently, upon interaction between MOS-based sensors and H<sub>2</sub> followed by re-exposure to air, atmospheric

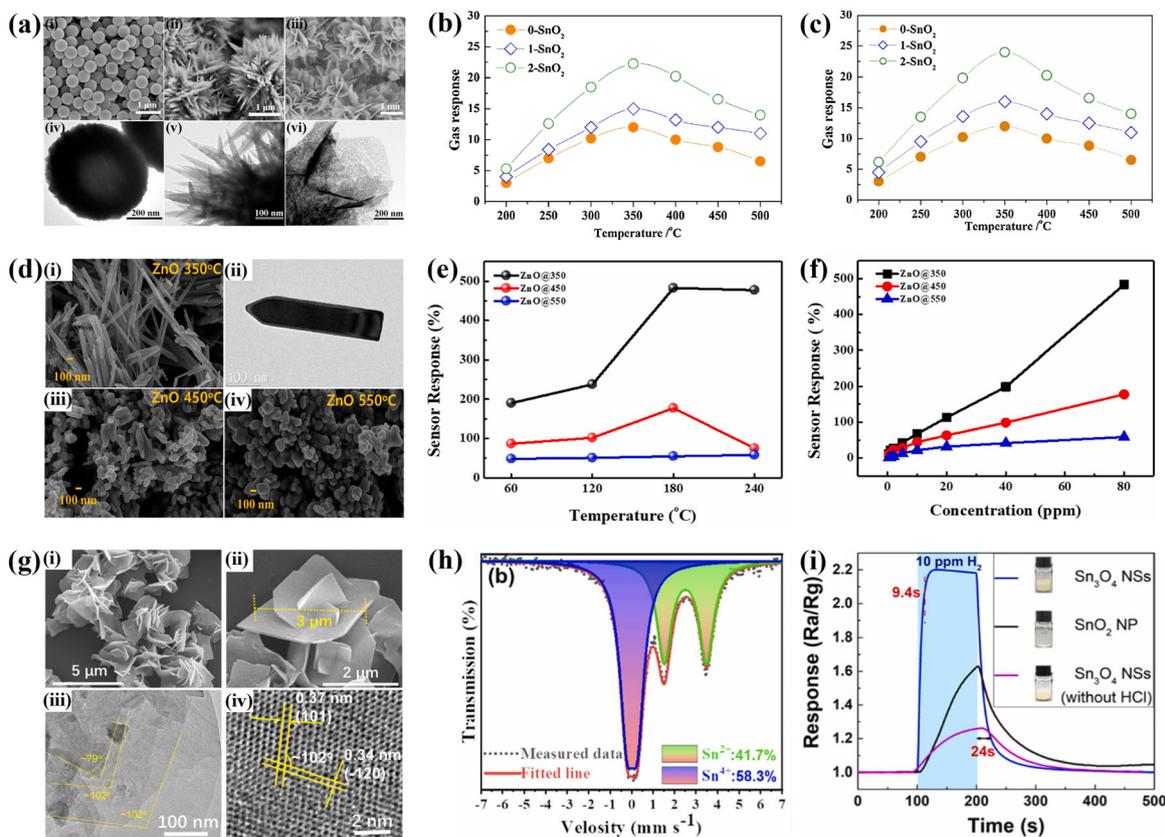
oxygen is reabsorbed to capture electrons from the conduction band, resulting in chemisorbed oxygen generation on the surface of the material and subsequent restoration of the surface space charge layer.<sup>11,62</sup> Therefore, it is imperative for both n-type and p-type MOS-based materials to possess a large surface area and a high reactivity to analytes, thereby augmenting their sensing properties.<sup>63</sup>

### 3.2. MOS nanostructures

It is worth noting that MOS-based sensors rely on the gas–solid interfacial reaction between the target gas and the active sites on the surface of MOS, and thus the precise structural engineering of MOSs in terms of size and shape plays a crucial role in enhancing sensor properties. Consequently, many researchers have dedicated themselves to designing MOS-based nanostructures. At present, the common morphology design of MOS-based sensing materials includes nanoparticles,<sup>64</sup> nanospheres,<sup>65</sup> nanowires,<sup>66</sup> nanorods,<sup>67</sup> nanofilms,<sup>68</sup> nanosheets,<sup>69</sup> and nanoflowers.<sup>70</sup>

Among them, NPs and nanospheres exhibit high surface-to-volume ratios; however, their tendency to agglomerate can lead to a reduction in active sites. For instance, Zhu *et al.*<sup>65</sup> studied the effects of three representative nanostructures on H<sub>2</sub> sensing behaviors. As shown in Fig. 5a(i)–(iii), the three nanostructures namely solid spheres (0-SnO<sub>2</sub>), nanoneedle-assembled nano urchins (1-SnO<sub>2</sub>), and nanosheet-assembled nanoflowers (2-SnO<sub>2</sub>) were synthesized by a facile hydrothermal method. The three SnO<sub>2</sub>-based sensors were exposed to 400 ppm H<sub>2</sub> at different operating temperatures from 200 to 500 °C in air, and the highest responses for 0-SnO<sub>2</sub>, 1-SnO<sub>2</sub>, and 2-SnO<sub>2</sub> were estimated to be 12, 15, and 22 at the optimal operating temperature of 350 °C (Fig. 5b). Among them, the nanosheet-assembled nanoflowers displayed superior sensing performance owing to their abundant active absorption sites, whereas the solid spheres showed the lowest sensitivity due to their densely packed structures. Interestingly, it was observed that the three sensors demonstrated enhanced sensitivity under vacuum at the same conditions compared to the atmospheric environment (Fig. 5c). The first principles calculations revealed that the H<sub>2</sub> molecule preferred to directly adsorb on the surface of SnO<sub>2</sub> and transferred more electrons. According to the above results, it was revealed that a direct interaction between H<sub>2</sub> and SnO<sub>2</sub> took place in the absence of oxygen.

Additionally, one-dimensional (1D) nanostructures have garnered significant attention owing to their high surface-to-volume ratios and high porosity, including nanofibers, nanowires, and nanorods. Recently, Tran *et al.*<sup>67</sup> demonstrated the role of aspect-ratio-controlled shape/size ZnO nanorods in H<sub>2</sub> sensing. As depicted in Fig. 5d, the three different aspect-ratio-controlled ZnO nanorods were synthesized by the thermal decomposition method at various annealing temperatures (350, 450, and 550 °C), and the aspect ratio decreased with increasing temperature. The ZnO nanorods synthesized through thermal decomposition at 350 °C exhibited the highest aspect ratio (~6.25) among all tested samples, which demonstrated superior H<sub>2</sub> sensing capabilities with a response of approximately 483% to 80 ppm H<sub>2</sub> at 180 °C (Fig. 5e and f). Hence, the enhanced H<sub>2</sub> sensing response of the ZnO@350



**Fig. 5** (a) SEM and TEM images of  $\text{SnO}_2$  samples: (i) and (iv) solid spheres, (ii) and (v) nanoneedle-assembled nano urchins, and (iii) and (vi) nanosheet-assembled nanoflowers. (b) Response of the three sensors exposed to 400 ppm  $\text{H}_2$  at different operating temperatures (from 200 to 500 °C) in air. (c) Response of the three sensors exposed to 400 ppm  $\text{H}_2$  at different operating temperatures (from 200 to 500 °C) in a vacuum. Reproduced with permission from ref. 65. Copyright 2018 Elsevier. (d) SEM and TEM images of aspect-ratio-controlled ZnO nanostructures: (i) and (ii) ZnO@350, (iii) ZnO@450, and (iv) ZnO@550. (e) Response of aspect-ratio-controlled ZnO nanostructures to 80 ppm  $\text{H}_2$  at different operating temperatures from 60 to 240 °C. (f) Response of aspect-ratio-controlled ZnO nanostructures to different  $\text{H}_2$  concentrations from 0.5 to 80 ppm at the optimal operating temperature of each sensor (ZnO@350 and ZnO@450: at 180 °C; ZnO@550: at 240 °C). Reproduced with permission from ref. 67. Copyright 2024 Elsevier. (g) (i) and (ii) SEM images of  $\text{Sn}_3\text{O}_4$  nanosheets at different magnifications, (iii) TEM image of  $\text{Sn}_3\text{O}_4$  nanosheets, (iv) HRTEM image of  $\text{Sn}_3\text{O}_4$  nanosheets. (h) Room-temperature Sn Mössbauer spectroscopy. (i) Response–recovery curves of pristine and  $\text{Sn}^{2+}$ -deficient  $\text{Sn}_3\text{O}_4$  as well as commercial  $\text{SnO}_2$  towards 10 ppm  $\text{H}_2$ . Reproduced with permission from ref. 69. Copyright 2024 Elsevier.

sensor can primarily be attributed to its high aspect ratio morphology, which promoted the formation of oxygen vacancies and provided a greater number of active sites for gas adsorption.

Furthermore, Liu *et al.*<sup>69</sup> developed ultra large  $\text{Sn}_3\text{O}_4$  nanosheet hierarchies with (010)-facet exposure and surface  $\text{Sn}^{2+}$ -deficiency *via* a facile hydrothermal method, which displayed excellent  $\text{H}_2$  sensing performance due to the thermodynamical stability in the  $\text{SnO}$  phase and the existence of oxygen vacancies. Fig. 5g revealed that the  $\text{Sn}_3\text{O}_4$  nanosheets with ultra-large two-dimensional (2D) structures were hierarchically assembled into a flower-like morphology and reflected the crystal growth orientation. It was confirmed that the exposed surface can be indexed as the (010) facet because the two sets of lattice fringes with *d*-spacings of 0.37 nm and 0.34 nm can be correspondingly indexed to the (101) and (−102) planes of the monoclinic  $\text{Sn}_3\text{O}_4$  (Fig. 5g(iv)). Furthermore, as shown in Fig. 5h, the atomic ratio of  $\text{Sn}^{2+}/\text{Sn}^{4+}$  was approximately 41.7/58.3, demonstrating the deficiency of  $\text{Sn}^{2+}$  in  $\text{Sn}_3\text{O}_4$ , which can

be attributed to etching of HCl. Finally, they compared the  $\text{H}_2$  sensing performance of the pristine and  $\text{Sn}^{2+}$ -deficient  $\text{Sn}_3\text{O}_4$  nanosheets as well as the commercial  $\text{SnO}_2$  nanopowders when exposed to 10 ppm  $\text{H}_2$ . The results showed that the  $\text{Sn}^{2+}$ -deficient  $\text{Sn}_3\text{O}_4$  nanosheets consistently exhibited superior sensitivity and response/recovery speed compared to the other samples (Fig. 5i). Herein, the hierarchical structure of the  $\text{Sn}_3\text{O}_4$  nanosheets facilitated rapid gas–solid interfacial contact reactions and fast release of target gases, while the  $\text{Sn}^{2+}$ -deficient (010) surface of  $\text{Sn}_3\text{O}_4$  nanosheets offered abundant active adsorption sites for  $\text{H}_2$  molecules. Therefore, the nanofilms or nanosheets have been used for  $\text{H}_2$  sensing due to their large lateral size with numerous active absorption sites.

However, the challenges of low sensitivity, poor selectivity, and high operating temperature persist in pure MOS nanostructure-based  $\text{H}_2$  sensors. Therefore, it is imperative to explore alternative approaches for enhancing sensor performance and minimizing energy consumption to align with the operational demands of the industry.

### 3.3. Modification of noble metal nanoparticles

The utilization of noble metal NPs (such as Pd,<sup>71</sup> Pt,<sup>72</sup> Au,<sup>73,74</sup> and Ag<sup>75</sup>) for the functionalization of MOSSs represents an efficacious approach to augment the response and selectivity of resistive H<sub>2</sub> sensors based on MOSSs. The modification of MOSSs by noble metal NPs is predicated upon two fundamental mechanisms: chemical sensitization and electron sensitization, namely, the spillover effect and the Fermi-level control sensitization mechanism, respectively.<sup>76,77</sup>

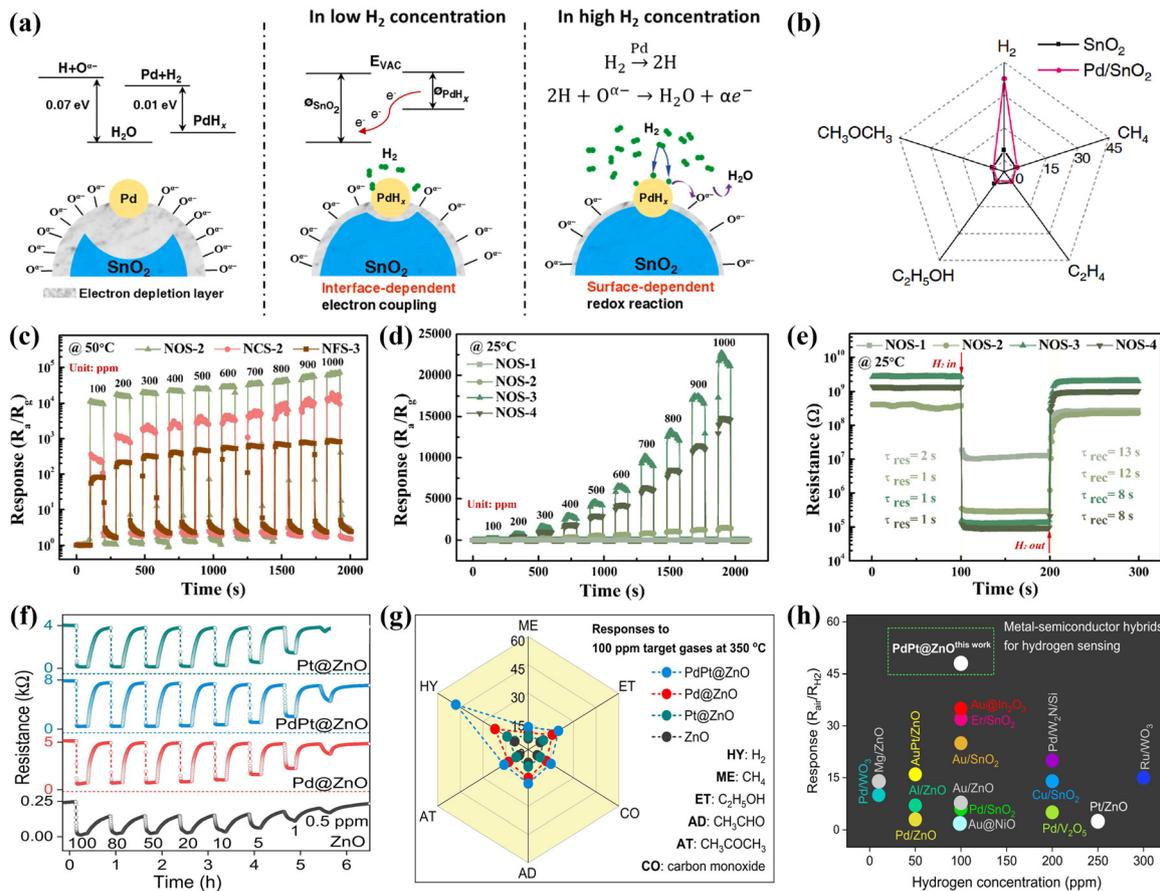
Chemical sensitization is used to describe the process in which gas molecules are dissociated by metal NPs (*e.g.* Pd, Pt, and Au) and then spill over onto the surface of MOSSs. Reducing the activation energy of the reaction effectively promotes the progress of the reaction without altering the intrinsic resistance of MOSSs.<sup>78</sup> In particular, sometimes H<sub>2</sub> are dissociated into H<sup>+</sup> and electrons in the presence of catalysts, which are then intercalated into MOSSs. This so-called “spillover” effect is well reported in MoO<sub>3</sub>, WO<sub>3</sub>, and V<sub>2</sub>O<sub>5</sub>.<sup>79–82</sup> Therefore, H<sub>2</sub> reactions on the surface of MOSSs are effectively promoted by metal NPs, thereby enhancing H<sub>2</sub> sensing properties. On the other hand, electronic sensitization is generated through the electron interaction between metal NPs (*e.g.* Pd, Ag, and Cu) and the interface of MOSSs. Upon exposure to air, the electronic sensitizers in the oxidized state act as strong acceptors of electrons that trap electrons from MOSSs and generate a large amount of adsorbed oxygen on their surfaces, inducing a surface space charge layer which is strongly depletive of electrons in the MOSSs near the interface.<sup>78,83</sup> However, when exposed to H<sub>2</sub>, the electronic sensitizers are reduced back to their metallic states, causing relaxation of the space charge layer by giving electrons back to MOSSs and resulting in a substantial resistance variation. The gas sensing performance of MOS-based sensors can be effectively enhanced by these two mechanisms involving metal NPs.

Among various noble metals, Pd and Pt are widely used as chemical sensitizers due to their excellent ability to induce the spillover effect of H<sub>2</sub> molecules onto MOSSs for H<sub>2</sub> sensing. For instance, Cheng *et al.*<sup>84</sup> demonstrated that Pt decoration can greatly improve the ZnO sensor performance both in dry and humid environments due to the spillover effect, and Amit *et al.*<sup>85</sup> reported the significant contribution of Pd in augmenting the H<sub>2</sub> sensing performance of V<sub>2</sub>O<sub>5</sub> through the spillover effect. In addition, Pd can also be used as an electronic sensitizer for MOS-based resistive H<sub>2</sub> gas sensors. In the presence of ambient air, oxygen adsorption on the surface of Pd leads to partial oxidation of metallic Pd into PdO. Consequently, the PdO as a potent electron acceptor induces an expanded surface space charge layer, resulting in electron depletion near the interface and giving rise to the formation of an electron depletion layer. In an H<sub>2</sub> environment, PdO is reduced back to Pd, releasing electrons that subsequently react with H<sub>2</sub> to form PdH<sub>x</sub>. The combination of PdO, Pd or PdH<sub>x</sub> with MOSSs forms different heterojunctions that modulate electron transfer. For example, Meng *et al.*<sup>83</sup> observed that Pd existed in the forms of PdO, Pd, and PdH<sub>x</sub> in different environments. Amongst others, PdO was a p-type semiconductor with a work function of 7.9 eV. Upon loading PdO onto the surface of n-type SnO<sub>2</sub>, an electron transfer

occurred from SnO<sub>2</sub> to PdO due to the lower work function of SnO<sub>2</sub> (4.5 eV), resulting in the formation of a p–n heterojunction. Therefore, the working temperature decreased from 300 to 125 °C and the sensitivity remarkably upgraded after Pd loading in SnO<sub>2</sub>. Furthermore, in most cases, there is a strong correlation between chemical sensitization and electronic sensitization, which synergistically enhances the gas sensing performance of MOSSs. For instance, Liu *et al.*<sup>86</sup> fabricated a H<sub>2</sub> sensor based on Pd/SnO<sub>2</sub> and demonstrated the coexistence of both sensitization mechanisms in gas sensing reactions, which exhibited a pronounced dependence on the concentration of H<sub>2</sub>. When the H<sub>2</sub> concentration was less than 1%, the electronic coupling effect at the PdH<sub>x</sub> and SnO<sub>2</sub> interfaces became predominant (Fig. 6a). Upon a further increase in H<sub>2</sub> concentration, the main mechanism was the redox reaction between H<sub>2</sub> and O<sup>z-</sup> on the surface of SnO<sub>2</sub> (Fig. 6a). The loading of Pd effectively reduced the activation energy of the reaction, which significantly improved the sensor's kinetic performance. Furthermore, a significant decrease in its sensitivity to additional disruptive gases was observed, indicating an elevated degree of selectivity (Fig. 6b). Therefore, diverse MOSSs, including SnO<sub>2</sub>,<sup>87</sup> ZnO,<sup>84</sup> In<sub>2</sub>O<sub>3</sub>,<sup>73</sup> TiO<sub>2</sub>,<sup>72,88</sup> WO<sub>3</sub>,<sup>89</sup> and V<sub>2</sub>O<sub>5</sub>,<sup>85</sup> functionalized by Pt, Pd, or Au, have been reported for selective H<sub>2</sub> sensing layers so far.

In particular, compared with widely used Pd NPs, bimetallic NPs demonstrate higher electro-catalytic characteristics due to their specific structure and the synergism of two components.<sup>91</sup> At present, the commonly used bimetallic catalysts are PdPt,<sup>92</sup> PdAu,<sup>93</sup> PdAg,<sup>94</sup> PtAu,<sup>95,96</sup> PtAg,<sup>97</sup> and AgAu<sup>97</sup> *etc.* For example, Meng *et al.*<sup>45</sup> proposed that PdPt/SnO<sub>2</sub> materials exhibited shape-dependent H<sub>2</sub> sensing performances due to the different morphologies of the PdPt sensitizer, such as nano-octahedrons, nanocubes and nanoflowers. Amongst others, the nano-octahedron modified SnO<sub>2</sub> (NOS) exhibited ultrahigh response (22821) and superfast response/recovery time (1/8 s) towards 1000 ppm H<sub>2</sub> at 25 °C, which was superior to the MOS-based H<sub>2</sub> sensing materials reported so far in terms of working temperature, response speed and response value (Fig. 6c–e). Kumar *et al.*<sup>94</sup> demonstrated that the sensor with a 1:1 Ag: Pd/ZnO has shown a high response of 51.36 towards 100 ppm of H<sub>2</sub> at an operating temperature of 275 °C. Consequently, the bimetallic NPs can efficiently increase the response value and decrease the operating temperature.

However, the decorated metal NPs on the surface of MOSSs tend to undergo facile aggregation and delamination from the MOS-based materials.<sup>98</sup> In particular, the surfaces of metal NPs can be easily poisoned by many chemicals that contain sulfur (H<sub>2</sub>S, SO<sub>2</sub>, and thiols) or phosphorus.<sup>99</sup> Therefore, the metal@oxide core-shell nanostructures can overcome the above-mentioned drawbacks. In this context, core-shell sensing materials can offer a substantial increase in surface area, structural stability, enhanced activities, and synergistic properties.<sup>100</sup> For instance, Nguyen *et al.*<sup>90</sup> reported that PdPt@ZnO core-shell nanoparticles (CSNPs) exhibited impressive H<sub>2</sub> sensing performances. The results showed that the PdPt@ZnO sensor displayed a high response of 48 with respect to Pd@ZnO (22), Pt@ZnO (14), and free ZnO (9), along with fast response and recovery times (0.7 and 3 min) to 100 ppm H<sub>2</sub> at 350 °C. Here, the various core-shell sensors all exhibited a higher



**Fig. 6** (a) Schematic illustration of a model for the change in reception and transduction mechanisms for Pd/SnO<sub>2</sub> films. (b) Selectivity of SnO<sub>2</sub> and Pd/SnO<sub>2</sub> to H<sub>2</sub> in comparison with interfering gases including CH<sub>3</sub>OCH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>OH, C<sub>2</sub>H<sub>4</sub> and CH<sub>4</sub>. Reproduced with permission from ref. 86. Copyright 2024 Elsevier. (c) Response–recovery curves of NOS-2, NCS-2 and NFS-3 to different H<sub>2</sub> concentrations ranging from 100 to 1000 ppm at 50 °C. (d) Response–recovery curves for NOS-1, NOS-2, NOS-3 and NOS-4 of different H<sub>2</sub> concentrations from 100 to 1000 ppm at 25 °C. (e) Response/recovery times for NOS-1, NOS-2, NOS-3 and NOS-4 to 1000 ppm H<sub>2</sub> at 25 °C. Reproduced with permission from ref. 45. Copyright 2023 Elsevier. (f) The dynamic sensing responses of the pure ZnO, Pd@ZnO, PdPt@ZnO, and Pt@ZnO CSNP sensors of varied H<sub>2</sub> concentration from 0.5 to 100 ppm at 350 °C. (g) Selectivity of pure ZnO, Pd@ZnO, Pt@ZnO, and PdPt@ZnO sensors to 100 ppm H<sub>2</sub> at 350 °C in comparison with interfering gases including CH<sub>4</sub>, C<sub>2</sub>H<sub>5</sub>OH, CH<sub>3</sub>CHO, CH<sub>3</sub>COCH<sub>3</sub>, and CO. (h) A comparison with recently reported advanced sensors based on different types of single metal NP decorated MOSSs in terms of H<sub>2</sub> sensing performance. Reproduced with permission from ref. 90. Copyright 2022 Elsevier.

response towards each of the tested target gases (especially towards H<sub>2</sub>) compared to that of the pure ZnO (Fig. 6f and g). Further, the superiority of the PdPt@ZnO CSNPs over other previously reported devices for H<sub>2</sub> detection was indicated in Fig. 6h. The observed enhancements can be ascribed to several factors: (1) the exceptional catalytic activity of the alloyed PdPt core, (2) the abundant presence of oxygen vacancies and chemisorbed oxygen in the ZnO shell, (3) the facile two-way transfer of electrons between the core and shell, and (4) the substantial surface area and porosity exhibited by CSNPs. From this perspective, diverse core–shell nanostructures based on MOSSs have been reported as highly sensitive and selective H<sub>2</sub> sensing layers.<sup>90,101,102</sup>

### 3.4. Doping of elements

Many investigations have indicated that doping of elements can significantly influence the morphology, crystal structure, adsorption capacity, and electrical properties of materials, thus serving as a prevalent strategy to enhance the gas-sensing

performance of MOSSs. In particular, when elements enter the lattice of MOS as acceptor or donor impurities, they induce a shift in the Fermi level and consequently change the band structure.<sup>103</sup> For n-type semiconductors, the Fermi level shifts up after the introduction of the donor impurity (providing electrons), because the donor impurity can introduce a set of fully occupied energy levels in the forbidden band near the conduction band, known as the donor level. Electrons at this level can readily transition to the conduction band, facilitating electrical conductivity. For p-type semiconductors, upon introducing an acceptor impurity (providing holes), there is a downward movement of the Fermi level. This is because the acceptor impurity introduces a set of completely unoccupied energy levels within the forbidden band close to the valence band, referred to as the acceptor level. Electrons in the valence band can easily transition to this level, leaving behind holes that contribute to conductivity in the valence band. So far, numerous MOSSs doped by various elements have

been developed, including  $\text{SnO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CuO}$ ,  $\text{ZnO}$ , and  $\text{TiO}_2$ .<sup>104–109</sup>

For example, Li *et al.*<sup>105</sup> employed the electrospinning and calcination technique to incorporate  $\text{La}^{3+}$  ions into  $\text{SnO}_2$  nanofibers at varying atomic molar ratio (AMR) concerning Sn. They found that the introduction of La changes the grain size of  $\text{SnO}_2$ . The average grain sizes of  $\text{SnO}_2$  nanofibers and La-doped  $\text{SnO}_2$  nanofibers (Fig. 7a) were calculated to be 11.9 nm (AMR 0), 11.5 nm (AMR 0.5%), 11.4 nm (AMR 1%) and 11.7 nm (AMR 3%), respectively. And all the La-doped  $\text{SnO}_2$  showed higher sensitivity than pristine  $\text{SnO}_2$  due to the polaron effect induced by La, which can provide fast dissociative adsorption of  $\text{H}_2$  on the surface (Fig. 7b). Among them, the sensor with 1% AMR exhibited the best  $\text{H}_2$  sensing performance (Fig. 7b and c). In addition, Hsiao *et al.*<sup>108</sup> developed five different doping concentrations ranging from 0 to 4% W to the  $\text{ZnO}$  structure to find an appropriate doping concentration in  $\text{H}_2$  sensing. As shown

in Fig. 7d, the grain structure was uniformly deposited on the surface (Fig. 7d(vi)), and with an increase in the doping concentration of W, the grain size of W-doped  $\text{ZnO}$  decreased correspondingly (Fig. 7d(i)–(v)) due to the smaller ionic radius of W (0.064 nm) compared to that of Zn (0.074 nm). Furthermore, the performance test results showed that the optimal doping concentration of W was 3% and the optimal working temperature was 150 °C (Fig. 7e). As depicted in Fig. 7f, the 3% W doped  $\text{ZnO}$  exhibited a high response of 67% for 100 ppm concentration of  $\text{H}_2$  at 150 °C. Herein, W served as a catalyst for enhancing the adsorption of oxygen species on the surface of  $\text{ZnO}$ .

In addition to affecting the morphology of materials, doped elements can also reduce the charge carrier concentration and affect the thickness of the material space charge layer by causing hole electron recombination in MOSSs, thus improving the sensor sensitivity.<sup>110</sup> For instance, Ai *et al.*<sup>106</sup> reported that

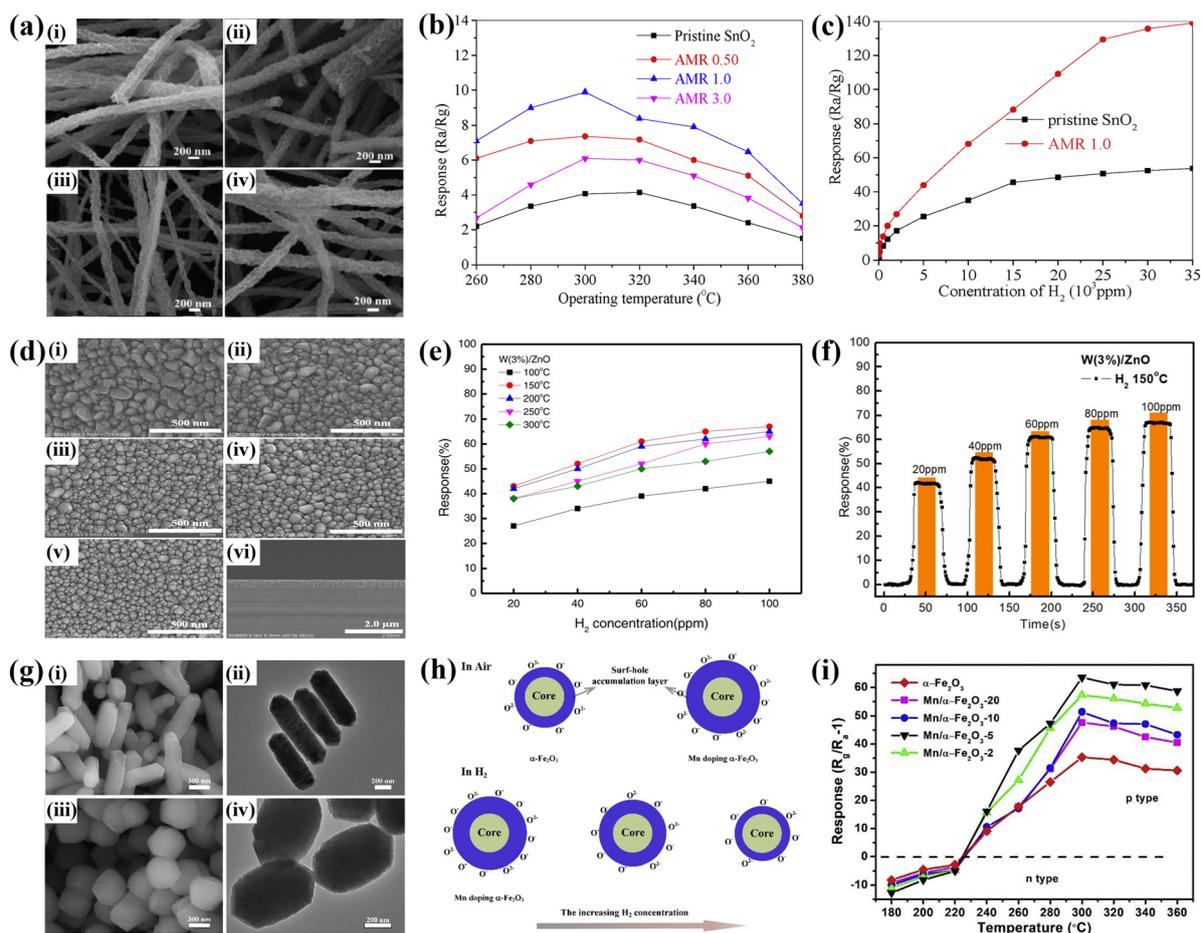


Fig. 7 (a) SEM images of the  $\text{SnO}_2$  nanofibers with La doping concentrations at (i) 0%, (ii) 0.5%, (iii) 1%, and (iv) 3%. (b) Response of  $\text{SnO}_2$  and La-doped  $\text{SnO}_2$  nanofibers to 100 ppm  $\text{H}_2$  at different operating temperatures. (c) Response of  $\text{SnO}_2$  and 1% La-doped  $\text{SnO}_2$  to different  $\text{H}_2$  concentrations from 5 to 35 000 ppm. Reproduced with permission from ref. 105. Copyright 2019 Elsevier. (d) SEM images of  $\text{ZnO}$  with W doping concentrations at (i) 0%, (ii) 1%, (iii) 2%, (iv) 3%, and (v) 4%. (vi) Cross-sectional image of W(4%)/ $\text{ZnO}$ . (e) Response of W(3%)/ $\text{ZnO}$  to  $\text{H}_2$  from 20 to 100 ppm at different temperatures. (f) Response–recovery curve of W(3%)/ $\text{ZnO}$  to different  $\text{H}_2$  concentrations ranging from 20 to 100 ppm at 150 °C. Reproduced with permission from ref. 108. Copyright 2023 Elsevier. (g) SEM and TEM images of  $\alpha\text{-Fe}_2\text{O}_3$  and Mn/ $\alpha\text{-Fe}_2\text{O}_3$ -5. (ii) SEM image of  $\alpha\text{-Fe}_2\text{O}_3$ , (iii) SEM image of Mn/ $\alpha\text{-Fe}_2\text{O}_3$ -5, (iv) TEM image of Mn/ $\alpha\text{-Fe}_2\text{O}_3$ -5. (h) Schematic diagram of the core/shell conductive structure of  $\alpha\text{-Fe}_2\text{O}_3$  and Mn doping of  $\alpha\text{-Fe}_2\text{O}_3$  in the air and Mn doping of  $\alpha\text{-Fe}_2\text{O}_3$  in different  $\text{H}_2$  concentrations. (i) Response of  $\alpha\text{-Fe}_2\text{O}_3$ , Mn/ $\alpha\text{-Fe}_2\text{O}_3$ -20, Mn/ $\alpha\text{-Fe}_2\text{O}_3$ -10, Mn/ $\alpha\text{-Fe}_2\text{O}_3$ -5, and Mn/ $\alpha\text{-Fe}_2\text{O}_3$ -2 to 200 ppm  $\text{H}_2$  with different temperatures. Reproduced with permission from ref. 106. Copyright 2022 Elsevier.

Mn-doped  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> synthesized by the hydrothermal method in H<sub>2</sub> sensing. Herein, the morphology of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> changed from rod to polyhedron by introducing Mn, as depicted in Fig. 7g. Furthermore, it was observed that the substitution of high-priced Fe ions with low-priced Mn ions led to the formation of a relatively high concentration of surface oxygen vacancy defects on the Mn/ $\alpha$ -Fe<sub>2</sub>O<sub>3-x</sub> nanoparticles. Consequently, compared to  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, Mn/ $\alpha$ -Fe<sub>2</sub>O<sub>3-x</sub> exhibited an increased adsorption capacity for oxygen ions (Fig. 7h). Upon exposure to H<sub>2</sub> gas, the trapped electrons were released into Mn/ $\alpha$ -Fe<sub>2</sub>O<sub>3-x</sub> through the reaction between H<sub>2</sub> molecules and adsorbed oxygen ions, resulting in a reduction in the thickness of the hole accumulation layer (Fig. 7h). Therefore, this change in carrier concentration caused by gas reactions resulted in a more significant alteration in sensor resistance and consequently enhanced gas response (Fig. 7i). Consequently, doping of elements can significantly improve the performance of MOS-based H<sub>2</sub> sensors in various aspects.

### 3.5. MOS-based composites

The incorporation of MOSs with other materials can improve the H<sub>2</sub> sensing properties due to their synergistic effect. The introduction of other materials into MOSs can lead to the formation of heterojunctions, which updates the charge distribution within the material and establishes a barrier at the material interface. This results in carrier depletion in one material and carrier accumulation in another, thereby significantly altering the total number of charge carriers present and enhancing both the sensitivity and selectivity of the sensor.<sup>11,111,112</sup>

Notably, the electronic properties of heterojunctions rely fundamentally on band alignment/bending and the accompanying charge transfer/separation. For semiconductor-semiconductor heterojunctions, three distinct types of band alignments exist, namely straddling (type I), staggered (type II), and broken gap (type III).<sup>113</sup> Regarding the type I band alignment, the conduction band minimum (CBM) and valence band maximum (VBM) of both semiconductor materials are straddled, making the two band edges of one material completely fall into another.<sup>113</sup> This results in the spontaneous transfer of electrons and holes from the large-bandgap material to the small-bandgap material, which improves the migration efficiency of charge carriers without providing additional energy, thereby

further enhancing the H<sub>2</sub> sensing performance (Fig. 8a). In the case of type II band alignment, there is a staggered arrangement of band edges between the two materials, resulting in only the CBM of one material falling within the bandgap of the other material.<sup>113</sup> Unlike type I band alignment, this alignment allows for effective spatial separation of holes and electrons as they are transferred to different materials, which significantly increases the concentration of charge carriers, thereby improving the sensitivity of H<sub>2</sub> sensors. The type III band alignment is characterized by a complete breaking of the band edges between the two materials, with the CBM of one material positioned lower than the VBM of the other material, indicating a partial overlap between their respective bands (Fig. 8c).<sup>113</sup> However, heterostructures with type III band characteristics are relatively rare due to the unique nature of band structures and there is no migration of electrons and holes between the two materials. Consequently, there are few research studies on hydrogen sensors based on type III heterojunctions.

To date, extensive reports have been published on the utilization of MOSs for forming heterojunctions to enhance the performance of H<sub>2</sub> sensors, including SnO<sub>2</sub>/Sb<sub>2</sub>O<sub>3</sub>,<sup>114</sup> SnO<sub>2</sub>/WO<sub>3</sub>,<sup>115</sup> SnO<sub>2</sub>/ZnO,<sup>116</sup> In<sub>2</sub>O<sub>3</sub>/ZnO,<sup>117</sup> and In<sub>2</sub>O<sub>3</sub>/SnO<sub>2</sub>.<sup>118</sup> For example, Wang *et al.*<sup>117</sup> investigated the effect of In<sub>2</sub>O<sub>3</sub> modified by ZnO with different weight percentages on H<sub>2</sub> sensing performance. As depicted in Fig. 9a, the ZnO synthesized by calcination of precursor ZIF-8 with a regular dodecahedral structure and the In<sub>2</sub>O<sub>3</sub> exhibited two different crystal phases, namely cubic phase c-In<sub>2</sub>O<sub>3</sub> (Inc) and hexagonal h-In<sub>2</sub>O<sub>3</sub> (Inh). The H<sub>2</sub> sensing performance test results demonstrated that the ZnO (5%)-Inc/Inh-based sensor exhibited the highest sensitivity at 450 °C when ZnO constituted 5 wt% of In<sub>2</sub>O<sub>3</sub> (Fig. 9b). Herein, the n-type In<sub>2</sub>O<sub>3</sub> and n-type ZnO formed a type II heterojunction, as shown in 7c. When exposed to H<sub>2</sub>, the adsorbed oxygen on the surface of ZnO (5%)-Inc/Inh reacted with H<sub>2</sub>, resulting in the release of electrons that effectively reduced the potential barrier and significantly enhanced the conductivity of the sensitive layer. Furthermore, the performance advantages of ZnO-Inc/Inh were investigated using density functional theory. The response of the composite system consisting of c-In<sub>2</sub>O<sub>3</sub> and h-In<sub>2</sub>O<sub>3</sub> to H<sub>2</sub> was theoretically more pronounced compared to that of the single crystalline phase In<sub>2</sub>O<sub>3</sub>. In addition, the incorporation of ZnO results in

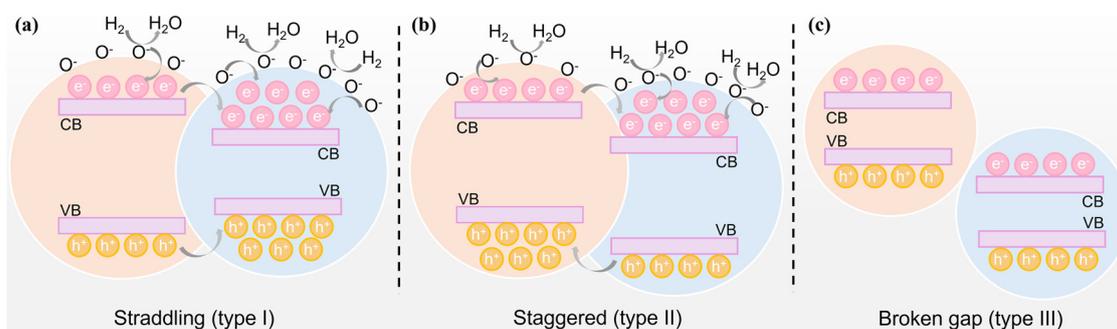
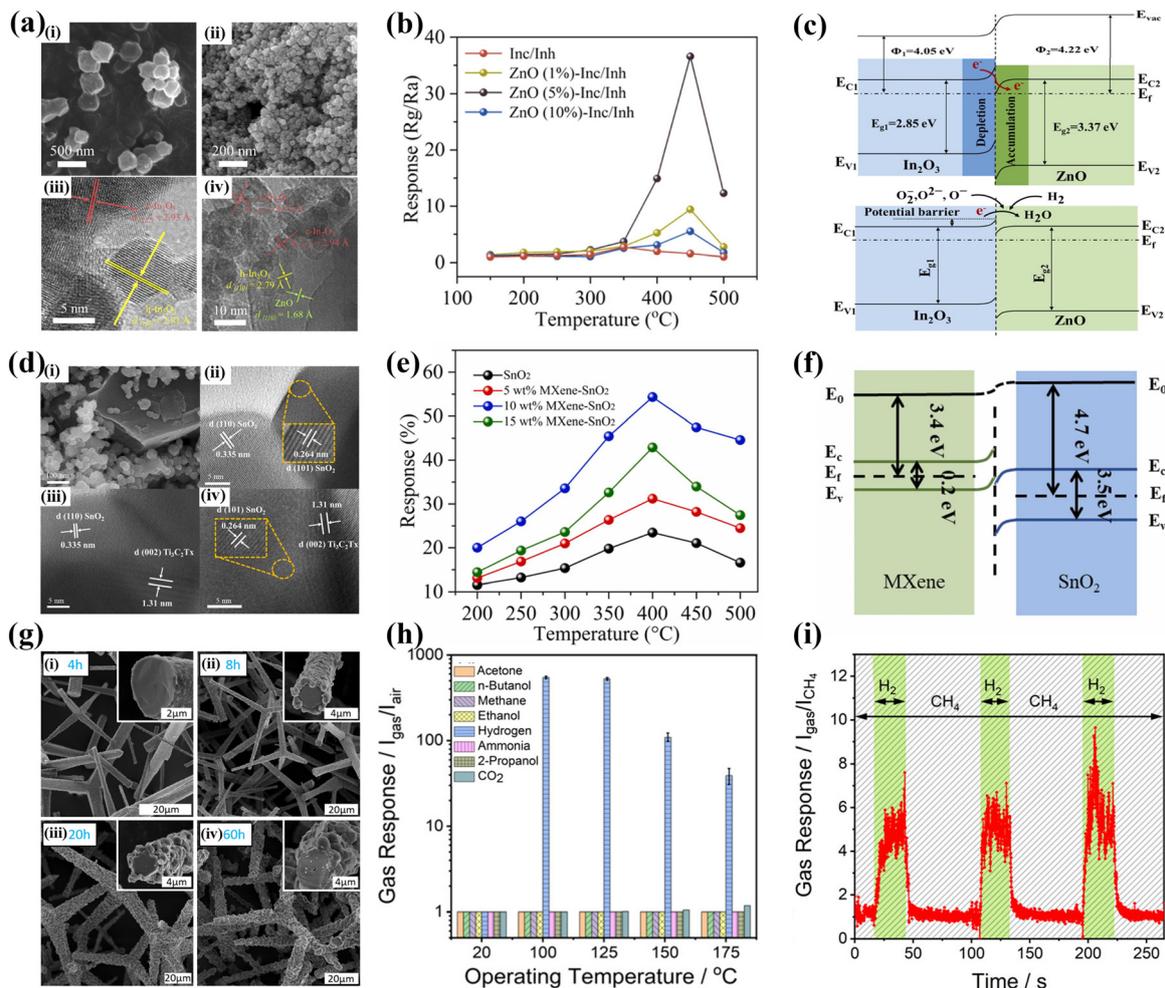


Fig. 8 Schematic of three types of heterojunctions. (a) Type of straddling. (b) Type of staggered. (c) Type of broken gap.



**Fig. 9** (a) SEM images of (i) ZnO and (ii) Inc/Inh; HRTEM images of (iii) Inc/Inh and (iv) ZnO-Inc/Inh. (b) Response of Inc/Inh-based sensors to 2000 ppm H<sub>2</sub> at different operating temperatures ranging from 100 to 500 °C. (c) Sensing mechanism of the heterojunction between In<sub>2</sub>O<sub>3</sub> and ZnO. Reproduced with permission from ref. 117. Copyright 2024 Elsevier. (d) (i) SEM image of 10 wt% MXene-SnO<sub>2</sub>, (ii) HRTEM image of SnO<sub>2</sub>, and (iii) and (iv) HRTEM image of 10 wt% MXene-SnO<sub>2</sub>. (e) Response of SnO<sub>2</sub>-based sensors to 600 ppm H<sub>2</sub> at different operating temperatures ranging from 200 to 500 °C. (f) Schematic diagram of the heterojunction between MXene and SnO<sub>2</sub>. Reproduced with permission from ref. 119. Copyright 2024 Elsevier. (g) SEM images of t-ZnO@ZIF-8 at different reaction times of 4, 8, 20, and 60 h. (h) Selectivity of the t-ZnO@ZIF-8 (4 h)-based sensor to 100 ppm of different gases at different operating temperatures on log<sub>10</sub> scales. (i) Response-recovery curve of t-ZnO@ZIF-8 (4 h) to 100 ppm H<sub>2</sub> in CH<sub>4</sub> at 100 °C. Reproduced with permission from ref. 120. Copyright 2023 American Chemical Society.

more pronounced charge transfer, variations in band gap, and alterations in the density of states in the composite, thereby indicating the presence of enhanced H<sub>2</sub> sensing performance.

In addition to MOS/MOS-based composites, the integration of MOSs with other materials can also give rise to heterojunctions, such as graphene,<sup>121</sup> MoS<sub>2</sub>,<sup>122</sup> WS<sub>2</sub>,<sup>123</sup> and MXene.<sup>119</sup> Recently, Chen *et al.*<sup>119</sup> compared the H<sub>2</sub> sensing performance of single SnO<sub>2</sub> and a MXene-SnO<sub>2</sub> composite. As illustrated in Fig. 9d, the connection between the hexagonal SnO<sub>2</sub> nanosheets and the MXene layered nanomaterial was well-established. Compared to the single SnO<sub>2</sub>-based sensor, all the MXene-SnO<sub>2</sub>-based sensors exhibited a significantly enhanced response to H<sub>2</sub>. Notably, among them, the 10 wt% MXene-SnO<sub>2</sub>-based sensor demonstrated the highest sensitivity at an optimal temperature of 400 °C (Fig. 9e). Herein, the p-type MXene and the n-type SnO<sub>2</sub> participated in the formation of p-n heterostructures in the

composite (Fig. 9f), which enhanced the H<sub>2</sub> sensing properties due to the strong interaction formed by the surface adsorption of the H<sub>2</sub> molecular heterojunction interface.

Moreover, the incorporation of MOFs with MOSs is commonly employed to enhance selectivity owing to their tunable pore sizes, which enables them to function as molecular sieves.<sup>120,124,125</sup> For instance, Poschmann *et al.*<sup>120</sup> reported a ZIF-8 functionalized single-crystalline tetrapodal ZnO gas sensor, which can detect H<sub>2</sub> in CH<sub>4</sub>. Amongst others, the formation of ZIF-8 was achieved through the reaction between ZnO tetrapods (t-ZnO) and evaporating 2-methylimidazole (HMeIM), followed by gas-phase crystallization to obtain t-ZnO@ZIF-8. As shown in Fig. 9g, the amount of ZIF-8 formed and the thickness of the ZIF-8 coating were significantly influenced by the reaction time, with a higher conversion of t-ZnO into ZIF-8 for observed longer reaction times. Among them, the t-ZnO@ZIF-8 (4 h) sample was

## Highlight

selected for gas sensing behavior study due to the decrease in surface area of tetrapod arm ends with increased reaction time, making electrical contact more challenging; additionally, thin MOF coatings can result in faster response/recovery speed. As depicted in Fig. 9h, the t-ZnO@ZIF-8 (4 h)-based sensor had no response for all tested gases at room temperature; however, with the operating temperature increasing, it exhibited extremely high response to H<sub>2</sub> with a high selectivity. The exceptional sensing performance can be summarized as follows: (1) ZIF-8 acted as a molecular sieve, enhancing the selectivity and sensitivity of t-ZnO to H<sub>2</sub>; (2) the formation of ZIF-8 introduced defects at the interface with t-ZnO, enabling modulation of the resistance of single crystalline ZnO by H<sub>2</sub> in the absence of atmospheric O<sub>2</sub>. Furthermore, they tested the response of a t-ZnO@ZIF-8 (4 h)-based sensor to 100 ppm H<sub>2</sub> in CH<sub>4</sub>. However, the presence of CH<sub>4</sub> did not affect the fast response to H<sub>2</sub> of the sensor. Therefore, it should also be feasible to quantify the concentration ratio of an H<sub>2</sub>/CH<sub>4</sub> mixture, rendering it a promising sensor for H<sub>2</sub> detection in natural gas pipelines. From this perspective, the introduction of selective sieving layers on MOSS is one of the most promising strategies to attain enhanced selectivity towards H<sub>2</sub>.

To date, the performance of MOS-based H<sub>2</sub> sensors has been significantly enhanced through various improvement methods. Table 2 summarizes the sensing characteristics of recently reported MOS-based H<sub>2</sub> sensors. The response values, response/recovery times, selectivity, long-term stability, and

detection limits of a few sensors have been demonstrated to be exceptional at room temperature. However, the practical applications of the majority of sensors are still hindered by their requirement for operation at high temperatures. At elevated operating temperatures, other gas molecules are also able to react with MOSS, leading to resistance changes and consequently compromising the selectivity of MOS-based sensors. Additionally, prolonged exposure to high temperatures can adversely impact the long-term stability of sensors by diminishing their sensitivity and shortening their lifespan. Furthermore, MOS-based sensors are also prone to the influence of H<sub>2</sub>O molecules in the surrounding environment. Hence, operating at near room temperature and exhibiting excellent humidity resistance in practical applications are essential for MOS-based H<sub>2</sub> sensors.

## 4. Others

### 4.1. Graphene

Graphene has gathered significant interest as a sensing material owing to its large specific surface area, high carrier mobility, high conductivity, and excellent physical and chemical properties.<sup>126</sup> It has been demonstrated that the gas sensing mechanism based on graphene heavily relies on physisorption.<sup>127</sup> Physisorption refers to the absorption of gas molecules onto the surface of sensing materials through intermolecular forces (van der Waals force) without forming chemical bonds, and the corresponding charge

Table 2 Summary of sensing properties of MOS-based H<sub>2</sub> sensors

Material	Morphology	Conc. (ppm)	Tem. (°C)	Res.	T <sub>res</sub> /T <sub>rec</sub> (s)	MDL (ppm)	Ref.
SnO <sub>2</sub>	Nanowires	150	250	54 <sup>a</sup>	19/45	0.5	66
ZnO	Nanorods	80	180	483% <sup>b</sup>	15.1/100.1	0.5	67
Sn <sub>3</sub> O <sub>4</sub>	Nanosheets	10	150	2.2 <sup>a</sup>	9.4/24	0.05	69
ZnO	Hollow hexahedron	300	250	101% <sup>b</sup>	611/1137	5	75
Pd/SnO <sub>2</sub>	Nanowires	40	150	8.5 <sup>a</sup>	6/3	—	66
Pd/CeO <sub>2</sub>	Hollow strings	10 000	RT	2.68% <sup>b</sup>	10/—	100	71
Pd/SnO <sub>2</sub>	Nanoparticles	500	125	254 <sup>a</sup>	1/22	10	83
Ag/ZnO	Hollow hexahedron	300	250	479% <sup>b</sup>	175/655	5	75
Pt/TiO <sub>2</sub>	Nanorods	1	RT	1.21 <sup>a</sup>	42/30	1	88
Pd/WO <sub>3</sub>	Nanoflowers	500	150	8658.98 <sup>a</sup>	1/3	20	89
Pd-Au/In <sub>2</sub> O <sub>3</sub>	Nanocubes	500	250	55 <sup>a</sup>	5/3	0.3	73
PdPt@In <sub>2</sub> O <sub>3</sub>	Spheres	100	RT	29.8 <sup>a</sup>	58/200	5	102
Ag-Pd/ZnO	Nanorods	100	275	51.36 <sup>a</sup>	—	—	94
PdPt@ZnO	Nanoparticles	100	350	48 <sup>a</sup>	0.7/180	0.5	90
Pd-Au@SnO <sub>2</sub>	Nanorods	100	175	46.4 <sup>a</sup>	19/302	25	93
Au@Pd/SnO <sub>2</sub>	Nanospheres	100	100	16.75 <sup>a</sup>	1/5	10	91
PdPt/SnO <sub>2</sub>	Nano-octahedrons	1000	RT	22821 <sup>a</sup>	1/8	100	45
Mn/α-Fe <sub>2</sub> O <sub>3</sub>	Polyhedrons	200	300	63.5 <sup>a</sup>	10/24	10	106
Cu/TiO <sub>2</sub>	Films	1000	200	2284% <sup>c</sup>	128/129	—	109
W/ZnO	Films	100	150	67% <sup>b</sup>	—	20	108
Cu/SnO <sub>2</sub>	Multilayer 3D	100	180	45% <sup>b</sup>	18/84	20	110
In <sub>2</sub> O <sub>3</sub> /SnO <sub>2</sub>	Nanofibers	50	350	3.5 <sup>a</sup>	1.1/1.9	50	118
SnO <sub>2</sub> /WO <sub>3</sub>	Spheres/plates	500	150	91% <sup>b</sup>	35/269	10	115
In <sub>2</sub> O <sub>3</sub> /ZnO	Nanoparticles/dodecahedrons	5000	450	79.91 <sup>a</sup>	1/6	0.053	117
SnO <sub>2</sub> /ZnO	Films	30	200	93 <sup>a</sup>	50/29	0.25	116
Pd-WO <sub>3</sub> /WS <sub>2</sub>	Nanoflowers	1000	125	4227.35 <sup>a</sup>	1/25	20	123
SnO <sub>2</sub> /MXene	Nanosheets	500	400	76% <sup>b</sup>	13/15	10	119
ZnO@ZIF-8	Tetrapods	100	100	546 <sup>d</sup>	2/2	5	120

Conc.: gas concentration; Tem.: operating temperature of the sensor; RT: room temperature (~25 °C); Res.: response of the sensor. <sup>a</sup> Response is defined as  $R_{\text{gas}}/R_{\text{air}}$ . <sup>b</sup> Response is defined as  $(R_{\text{gas}} - R_{\text{air}})/R_{\text{air}} \times 100\%$ . <sup>c</sup> Response is defined as  $(I_{\text{gas}} - I_{\text{air}})/I_{\text{air}} \times 100\%$ . <sup>d</sup> response is defined as  $I_{\text{gas}}/I_{\text{air}}$ ; T<sub>res</sub>: response time of the sensor; T<sub>rec</sub>: recovery time of the sensor; MDL: minimum detection limit of the sensor; Ref.: reference; —: not reported; 3D: three-dimensional.

transfer mechanism does not rely on the breakdown of the absorbed gas. Gas molecules absorb on the surface of graphene and act as electron donors or acceptors.<sup>127</sup> Herein, H<sub>2</sub> molecules serve as electron donors (Fig. 1c). It is worth noting that this absorption process can occur at low temperatures and in the absence of oxygen. However, it always requires the sensing material with a favorable surface adsorption energy value for the target gas molecules and optimal electronic band structure facilitating the charge transfer.<sup>128</sup> Additionally, physisorption exhibits some problems including poor reversibility and weak response magnitude. Based on these results, bare graphene is not great for H<sub>2</sub> sensing, so the introduction of catalysts to enhance the H<sub>2</sub> adsorption was crucially important.

So far, many H<sub>2</sub> sensors based on catalyst-functionalized graphene have been reported.<sup>129–132</sup> For instance, Zhu *et al.*<sup>129</sup> designed a flexible H<sub>2</sub> sensing film based on Pd nanoclusters/reduced graphene oxide (rGO) *via* one-step vacuum filtration.

Amongst others, the rGO/Pd film sensor demonstrated superior response, rapid response/recovery kinetics, and exceptional stability in comparison to the bare rGO film due to the pronounced catalytic effect of ultrasmall (3.3 nm) Pd nanoclusters. Besides, the rGO/Pd-based flexible film sensor achieved a stable response to 2% H<sub>2</sub> after different bending states and still maintained excellent sensing performance after suffering from repeated bending/recovery deformations (Fig. 10a–c).

However, limited research has been conducted on enhancing the sensing performance through structural modifications of graphene. According to some reports, graphene obtained through exfoliation and chemical vapor deposition (CVD) exhibits chemical inertness due to the absence of dangling bonds,<sup>135</sup> while the nanocomposites based on 2D graphene tend to aggregate owing to  $\pi$ - $\pi$  stacking and van der Waals forces acting between the layers of graphene.<sup>131,136,137</sup> These will all lead to the degradation of the H<sub>2</sub> sensing properties.

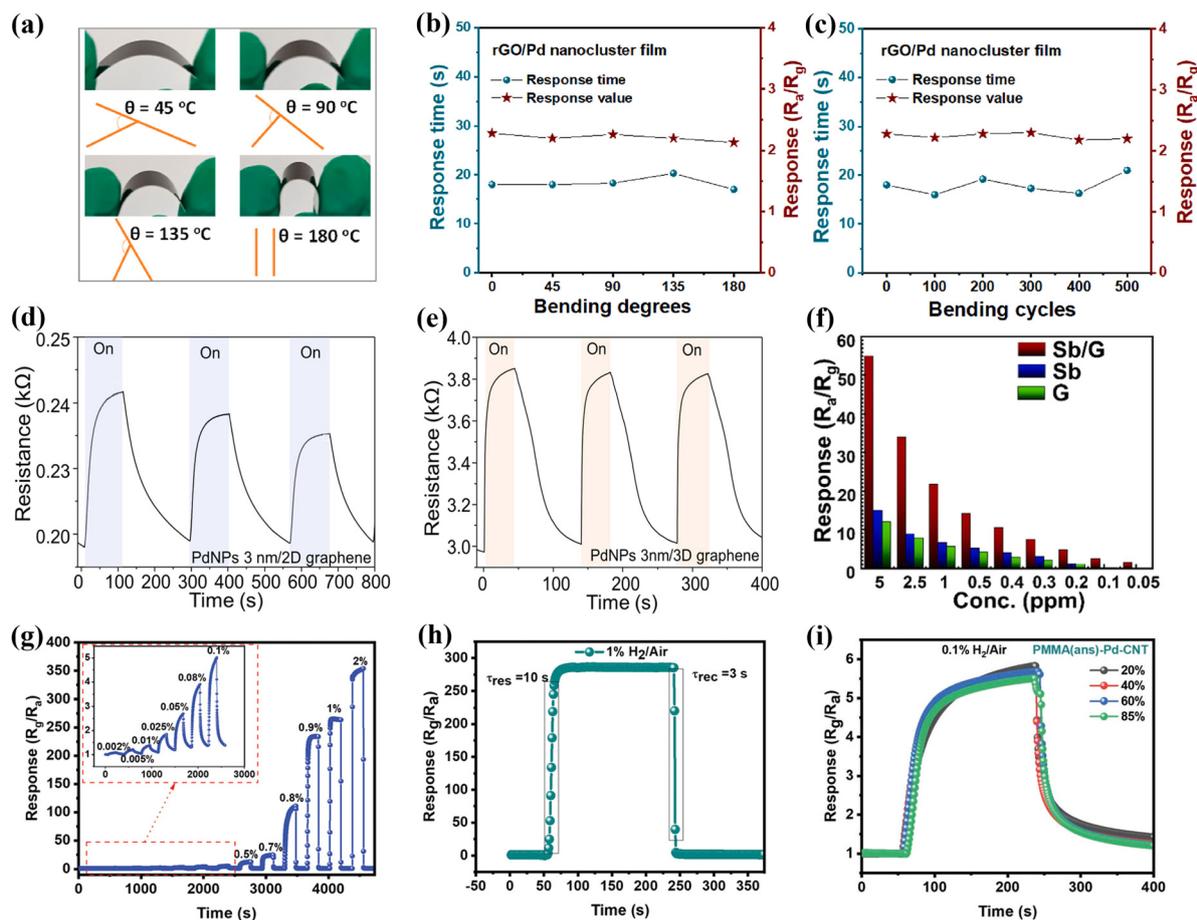


Fig. 10 (a) Photos of the rGO/Pd film at different bending degrees. (b) Response value and response time of the rGO/Pd-based sensor to 2% H<sub>2</sub> under different bending degrees at room temperature. (c) Response value and response time of the rGO/Pd-based sensor to 2% H<sub>2</sub> at room temperature after different bending cycles (one cycle: from 0° to 180° and back to 0°). Reproduced with permission from ref. 129. Copyright 2022 Elsevier. (d) Response–recovery curves of PdNPs (3 nm, the thickness of Pd layer)/2D graphene and (e) PdNPs (3 nm)/3D graphene to 3% H<sub>2</sub> at 30 °C. Reproduced with permission from ref. 131. Copyright 2024 Elsevier. (f) Response of Sb, Sb and Sb/G-based sensors to different H<sub>2</sub> concentrations ranging from 0.05–5 ppm at room temperature. Reproduced with permission from ref. 133. Copyright 2024 Elsevier. (g) The response–recovery curve of the PMMA-Pd-SWNT sensor to different H<sub>2</sub> concentrations ranging from 0.002–2% at room temperature. (h) Response/recovery time of the PMMA-Pd-SWNT sensor to 1% H<sub>2</sub> at room temperature. (i) Response–recovery curves of the PMMA-Pd-SWNT sensor for different humidity to 0.1% H<sub>2</sub> at room temperature. Reproduced with permission from ref. 134. Copyright 2023 Wiley-VCH GmbH.

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Thus, to take full advantage of graphene, it is important to modify the intrinsic 2D structure of graphene. Recently, Lee *et al.*<sup>131</sup> developed an H<sub>2</sub> sensor based on Pd-decorated 3D graphene, which was fabricated by introducing Cu vapor as the remote catalyst in a metal-organic CVD system to directly grow 3D graphene on 300 nm SiO<sub>2</sub>/Si substrates and decorating with thermally evaporated Pd NPs. As shown in Fig. 10d and e, when the same thickness of Pd NPs were deposited on 2D and 3D graphene, the 3D graphene demonstrated a higher response of 41.9% towards 3% H<sub>2</sub> at 30 °C because of the larger surface area and dense distribution of Pd NPs on 3D graphene than those of 2D graphene. Therefore, this study provides a new idea for the improvement of the H<sub>2</sub> sensing properties.

On the other hand, the heterostructures of graphene-based composites also display interesting H<sub>2</sub> sensing characteristics. In the heterostructures, graphene serves as a versatile platform, which not only possesses a huge specific surface area but also provides a highly conductive path for charge transport upon gas adsorption and desorption. For example, Kumar *et al.*<sup>133</sup> fabricated a class of heterostructures based on 2D Pnictogens and graphene by photolithography and pattern transfer methods for H<sub>2</sub> detection at room temperature. Amongst the Pnictogen class, antimonene/graphene (Sb/G) showed excellent H<sub>2</sub> sensing properties. As depicted in Fig. 10f, the Sb/G heterostructure displayed a superior response of 54.5 towards 5 ppm H<sub>2</sub> as compared to individual Sb (15.3) and G (12.1). Besides, it also showed short response/recovery time (12/34 s), low detection limit (50 ppb), high selectivity, and long-term stability. In a nutshell, the extraordinary H<sub>2</sub> sensing behavior can be ascribed to the heterostructure and electronic states, which provided a large density of active pathways, a high surface-to-volume ratio, and a tunable Schottky barrier. Thus, it provides the possibility to expand a novel family of Pnictogen-graphene sensors.

#### 4.2. CNTs

CNTs have been investigated for real-time detection of gases at room temperature due to their high-quality crystal lattices, tunable electrical properties, and chemical sensitivity.<sup>138,139</sup> However, similar to graphene, the bare CNTs have no appreciable interaction with H<sub>2</sub>, thus necessitating the exploration of suitable H<sub>2</sub> sensitive materials for CNTs functionalization.<sup>140</sup> To date, Pd is the most commonly employed catalyst for H<sub>2</sub> sensing due to its superior selectivity in absorbing H<sub>2</sub>, while conducting polymers are commonly used as molecular sieves.<sup>134,141–144</sup> Moreover, there are also reports available based on Pt/CNTs.<sup>145,146</sup> Typically, CNTs are employed to enhance the conductivity of the composites, thereby improving the efficiency of electron transport and aggregation. Additionally, they act as supporting frameworks for increasing the surface-to-volume ratio, providing more active sites and consequently enhancing the absorption of H<sub>2</sub>.<sup>147</sup>

Recently, Du *et al.*<sup>141</sup> constructed nanoarchitectures of Pd and poly-3, 4-ethylenedioxythiophene (PEDOT) coatings on multi-walled CNTs, which achieved dual H<sub>2</sub> and NH<sub>3</sub> detection. Herein, the multi-walled CNTs were used for both improving the surface ratio and assisting electron transfer. Notably, the

PEDOT@CNTs exhibited negligible sensitivity to H<sub>2</sub>, indicating that the presence of PEDOT wrapping on the CNTs did not directly influence H<sub>2</sub> sensing. Instead, the H<sub>2</sub> sensing capability of Pd&PEDOT@CNTs was primarily governed by the Pd NPs. Furthermore, it was also observed that the size distribution of the Pd NP coating on the CNTs also affected the H<sub>2</sub> sensing characteristics. In another case, Girma *et al.*<sup>134</sup> successfully fabricated reproducible and highly sensitive semiconducting single-walled carbon nanotube (SWNT) sensors by coating PMMA and decorating Pd. The uniform-density and monolayer SWNT films were synthesized using chemical immobilization through the click reaction between azide-functionalized polymer-wrapped SWNTs and immobilized alkyne polymer on a substrate before decorating with Pd nanoparticles (0.5–3.0 nm). As illustrated in Fig. 10g and h, the PMMA-Pd-SWNT sensor demonstrated a wide detection range of H<sub>2</sub> concentrations (0.002–2%) and a high response up to 285 at 1% H<sub>2</sub> with the response/recovery time of 10/3 s at room temperature. Amongst others, Pd efficiently reduced the activation energy of the surface reactions and enhanced the adsorption of H<sub>2</sub> and desorption of H<sub>2</sub>O molecules, while the PMMA layer greatly optimized the film morphology and reduced the apparent activation energy, contributing to a high response and a fast response/recovery speed. Furthermore, the introduction of the PMMA layer effectively prevented H<sub>2</sub>O molecules from diffusing and allowed H<sub>2</sub> permeation, which guaranteed stable operation at high humidity of the PMMA-Pd-SWNT sensor (Fig. 10i).

In addition to catalyst type and size distribution, the band gap of CNTs also exerts an influence on H<sub>2</sub> sensing performance. The difference in the band gap of CNTs will restrict the transition of electrons from the valence to the conduction band, resulting in an unequal number of holes in the valence band. For example, Zhang *et al.*<sup>144</sup> explored the effect of the diameters of SWNTs on H<sub>2</sub> detection. The results demonstrated that the response of the sensor with 0.7–1.2 nm SWNTs to 1 ppm H<sub>2</sub> was approximately 6 times compared to that of the one with 1.2–1.6 nm. That was because the wider band gap of 0.7–1.2 nm p-type SWNTs resulted in fewer holes in the valence band and easier depletion of holes by electrons from the dissociation of H<sub>2</sub>. Therefore, researchers can optimize the performance of CNT-based H<sub>2</sub> sensors from multiple perspectives, including type of catalysts, size distribution of catalysts, and band gap of CNTs.

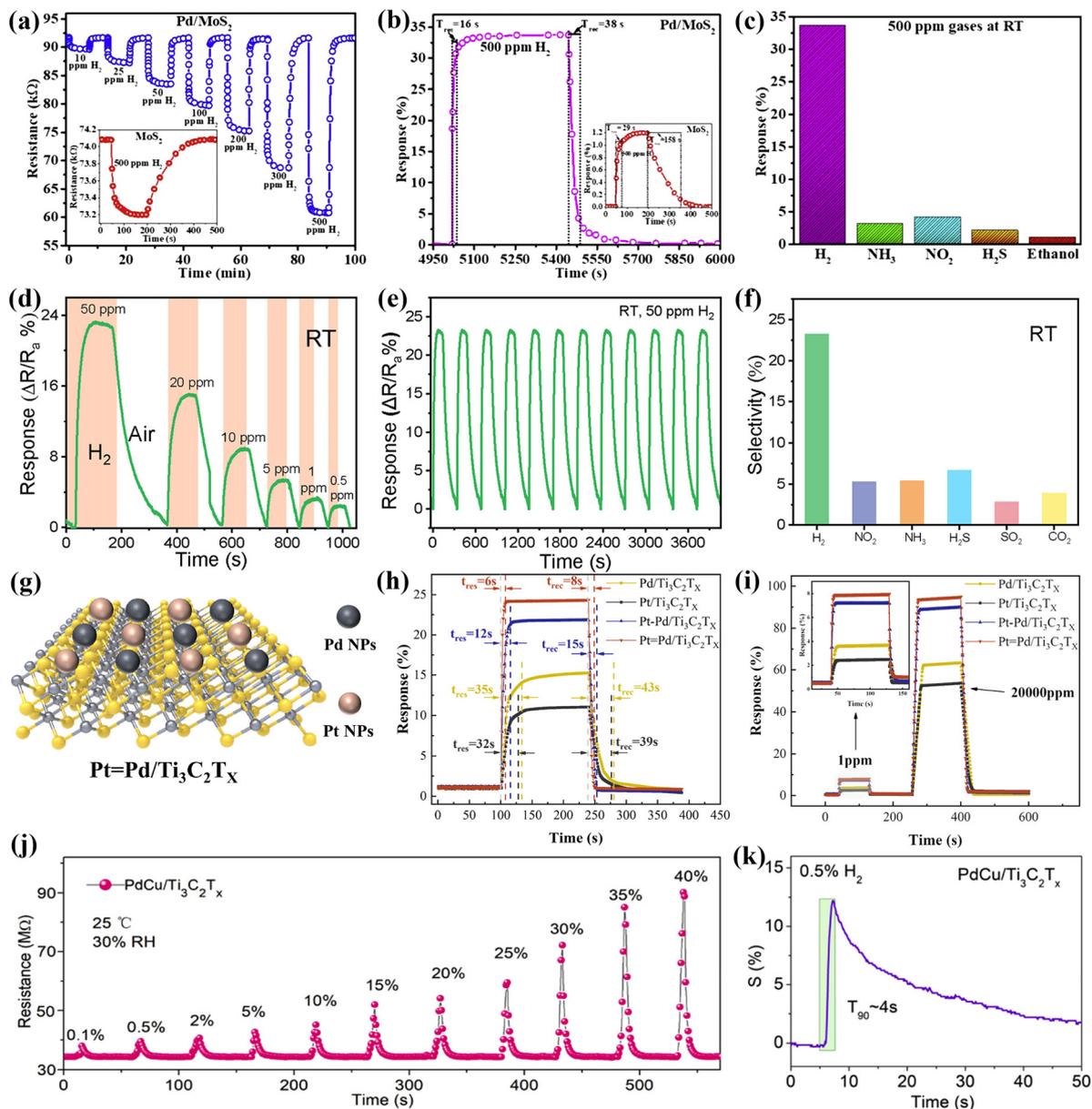
#### 4.3. TMDs

Recently, 2D TMDs have demonstrated great potential for gas detection at room temperature due to their high surface-to-volume ratio, high carrier mobility, and tunable electrical and chemical properties.<sup>148,149</sup> To date, numerous studies have demonstrated the physisorption of H<sub>2</sub> on the surface of TMDs at room temperature.<sup>128,150,151</sup> However, TMDs always display relatively lower adsorption energy compared to other gases (such as NO<sub>2</sub>, NO, CO, NH<sub>3</sub>, CH<sub>4</sub>, CO<sub>2</sub>),<sup>128,151</sup> which is not conducive to developing highly sensitive and selective H<sub>2</sub> sensors based on pure TMDs. Therefore, extensive investigations have been conducted to address this issue by researchers.

So far, many literatures have suggested that it is efficient to improve the TMD-based  $H_2$  sensing properties by combining catalysts with TMDs.<sup>152–154</sup>

For instance, Jiaswal *et al.*<sup>153</sup> reported a highly sensitive and selective  $H_2$  sensor based on Pd NP-functionalized  $MoS_2$  thin films. They prepared Pd/ $MoS_2$  thin films *via* a single-step DC

magnetron sputtering technique. As illustrated in Fig. 11a–c, compared to the pristine  $MoS_2$  sensor, the Pd/ $MoS_2$  sensor exhibited significantly enhanced  $H_2$  sensing characteristics, including a high response of 33.7%, fast response/recovery time of 16/38 s to 500 ppm  $H_2$  at room temperature, low detection limit of 1 ppm, and high  $H_2$  selectivity against  $NH_3$ ,



**Fig. 11** (a) Response–recovery curve of Pd/ $MoS_2$  to different  $H_2$  concentrations ranging from 10–500 ppm at room temperature; the inset shows a response–recovery curve of Pd/ $MoS_2$  to 500 ppm  $H_2$  at room temperature. (b) Response/recovery times of Pd/ $MoS_2$  and  $MoS_2$  to 500 ppm  $H_2$  at room temperature. (c) Selectivity of Pd/ $MoS_2$  to 500 ppm  $H_2$  in comparison with interfering gases including  $NH_3$ ,  $NO_2$ ,  $H_2S$ , and ethanol at room temperature. Reproduced with permission from ref. 153. Copyright 2020 Elsevier. (d) The response–recovery curve of Pt@ $MoS_2$  to different  $H_2$  concentrations ranging from 0.5–50 ppm. (e) Repeatability of Pt@ $MoS_2$  to 50 ppm  $H_2$  at room temperature. (f) Selectivity of Pt@ $MoS_2$  to 50 ppm  $H_2$  in comparison with interfering gases including  $NO_2$ ,  $NH_3$ ,  $H_2S$ ,  $SO_2$ , and  $CO_2$  at room temperature. Reproduced with permission from ref. 154. Copyright 2023 American Chemical Society. (g) Structure diagram of Pt = Pd/ $Ti_3C_2T_x$ . (h) Response/recovery times of  $Ti_3C_2T_x$ -based sensors to 200 ppm  $H_2$  at room temperature; Pt–Pd represents an alloy of Pt and Pd. (i) Response–recovery curves of  $Ti_3C_2T_x$ -based sensors to 1 ppm and 20 000 ppm  $H_2$ . Reproduced with permission from ref. 155. Copyright 2023 Elsevier. (j) Response–recovery curves of PdCu and PdCu/ $Ti_3C_2T_x$  to different  $H_2$  concentrations ranging from 0.5–4% at 25 °C. (k) Response–recovery curve of PdCu/ $Ti_3C_2T_x$  nanocomposites to different  $H_2$  concentrations ranging from 0.1–40% at 25 °C. Reproduced with permission from ref. 156. Copyright 2024 Elsevier.

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NO<sub>2</sub>, H<sub>2</sub>S, and ethanol. Therefore, the introduction of Pd NPs improved the sensing performance of MoS<sub>2</sub> owing to the catalytic activity of Pd and the creation of the Schottky barrier at the junction between Pd NPs and the MoS<sub>2</sub> semiconductor.

In addition to incorporating Pd NPs, Pt NPs were also integrated into 2D TMDs for the advancement of H<sub>2</sub> sensors. Wadhwa *et al.*<sup>154</sup> developed vertically aligned large-area MoS<sub>2</sub> flakes with enhanced H<sub>2</sub> sensing characteristics modified by Pt NPs. The presence of Pt NPs offered a surface reaction between H atoms and MoS<sub>2</sub> and supported the diffusion of H atoms into MoS<sub>2</sub>. As depicted in Fig. 11d, the Pt@MoS<sub>2</sub>-based sensor showed a high response of 23.2% to 50 ppm H<sub>2</sub> and an ultra-low detection limit of 0.5 ppm at room temperature, whereas the pristine MoS<sub>2</sub> only had a response of 9%. Besides, it displayed excellent repeatability and high selectivity (Fig. 11e and f). Therefore, it is imperative to modify TMDs with sensitizers, to develop TMD-based H<sub>2</sub> sensors with high sensing properties.

#### 4.4. MXenes

MXenes represent a class of ternary, layered, machinable transition metal carbide, nitride and carbon nitride two-dimensional materials, and their chemical formula is M<sub>n+1</sub>AX<sub>n</sub>, where *n* = 1, 2, or 3, “M” is an early transition metal, “A” is a group of A (mostly groups 13 and 14), and “X” is the C element or N element.<sup>157</sup> In particular, MXenes exhibit a narrow band gap, a large specific surface area, an abundance of surface functional groups, and a high electron transfer rate,<sup>157</sup> rendering them highly suitable for applications in the field of H<sub>2</sub> detection. Herein, the sensing mechanisms for MXenes are similar to the above-mentioned MOS-based H<sub>2</sub> sensors.

Charan *et al.*<sup>158</sup> synthesized Ti<sub>3</sub>C<sub>2</sub> nanosheets by selective etching of the Al layer from a prefabricated MAX phase (Ti<sub>3</sub>AlC<sub>2</sub>) precursor using hydrofluoric (HF) acid, which demonstrated a response of 1.24 with a response/recovery time of 32/125 s to 3000 ppm H<sub>2</sub> at room temperature. However, the pure MXene-based H<sub>2</sub> sensors usually present certain challenges including long response time, poor repeatability, and baseline drift.<sup>119,158</sup> Therefore, researchers have tried to employ metal NPs for the functionalization of MXenes or combine MXenes with other materials to

augment their H<sub>2</sub> sensing properties.<sup>155,156,159,160</sup> For instance, Wang *et al.*<sup>155</sup> prepared spatially separated Pt and Pd modified Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> (Pt = Pd/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>, Fig. 10g) by a hydrothermal chemical reduction, which displayed excellent sensing performance at room temperature. A comparison of H<sub>2</sub> sensing performance between four different Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>-based sensors modified by Pt, Pd, Pt-Pd alloy, and Pt = Pd respectively was shown in Fig. 11h and i. All of them exhibited high responses to different H<sub>2</sub> concentrations at room temperature, whereas the pure Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>-based sensor almost had no response to H<sub>2</sub>. Among them, the Pt = Pd/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub>-based sensor demonstrated the best sensing performance including the highest response value (24.6%) and the shortest response/recovery time (6/8 s) to 200 ppm H<sub>2</sub>. Besides, it also exhibited an ultra-low limit of detection of 1 ppm (Fig. 11i), good repeatability, long-term stability, and high selectivity. Herein, Pt can enhance the dispersion of the Pt = Pd owing to the strong metal-support interaction (SMSI) effect and Pd had high adsorption and dissociation activity for H<sub>2</sub>, so compared to monometallic-modified Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> the Pt = Pd/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> showed superior H<sub>2</sub> sensing performances. Additionally, the higher H<sub>2</sub> sensing capabilities of Pt = Pd/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> than Pt-Pd/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> can be ascribed to the alloy formation of Pt-Pd weakening the electron transfer.

In addition, Qiu *et al.*<sup>156</sup> reported a 3D PdCu-modified Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> nanocomposite prepared by a self-sacrificing template method. As depicted in Fig. 11j, compared to PdCu NPs, the PdCu/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> nanocomposites showed superior H<sub>2</sub> sensing behavior. Notably, the PdCu/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> nanocomposites exhibited consistent and stable response and recovery behaviors when exposed to a wide range of H<sub>2</sub> concentrations from 0.1 to 40% (Fig. 11k). Herein, the synergistic interaction and the heterostructure between PdCu NPs and Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> resulted in the outstanding sensing performance of the PdCu/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> nanocomposites. Based on these findings, the utilization of metal NPs for the functionalization of MXenes and their integration with other materials have demonstrated remarkable efficacy in enhancing their hydrogen sensing capabilities.

So far, emerging materials, including graphene, CNTs, TMDs, and MXens, have exhibited some advancements in the realm of H<sub>2</sub> sensing. Table 3 summarizes the sensing performance of these materials in recent years. The sensing performance of these

Table 3 Summary of the sensing properties of other H<sub>2</sub> sensors

Material	Conc.	Tem. (°C)	Res.	T <sub>res</sub> /T <sub>rec</sub> (s)	MDL (ppm)	Ref.
rGO/Pd	2%	RT	2.28 <sup>a</sup>	18/—	2500	129
Pd-GO	35 ppm	100	2.1% <sup>b</sup>	18/20	—	130
Sb/G	5 ppm	RT	54.5 <sup>a</sup>	12/34	0.05	133
PMMA-Pd-SWNT	1%	RT	285 <sup>c</sup>	10/3	20	134
Pd/HKUST-1/SWNT	1 ppm	RT	6.09 <sup>c</sup>	—/1	1	144
Pt/MoS <sub>2</sub>	1%	RT	8.7% <sup>b</sup>	8.1/16	500	152
Pd/MoS <sub>2</sub>	500 ppm	RT	33.7% <sup>b</sup>	16/38	10	153
Pt/MoS <sub>2</sub>	50 ppm	RT	23.2% <sup>b</sup>	33/121	0.5	154
Ti <sub>3</sub> C <sub>2</sub>	3000 ppm	RT	1.24 <sup>a</sup>	32/125	500	158
PdCu/Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub>	2%	RT	20% <sup>b</sup>	4/35	1000	156
Pt = Pd/Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub>	200 ppm	RT	24.6% <sup>b</sup>	6/8	1	155

Conc.: gas concentration; Tem.: operating temperature of the sensor; RT: room temperature (~25 °C); Res.: response of the sensor. <sup>a</sup> Response is defined as  $R_{\text{air}}/R_{\text{gas}}$ . <sup>b</sup> Response is defined as  $(R_{\text{gas}} - R_{\text{air}})/R_{\text{air}} \times 100\%$ . <sup>c</sup> Response is defined as  $R_{\text{gas}}/R_{\text{air}}$ ; T<sub>res</sub>: response time of the sensor; T<sub>rec</sub>: recovery time of the sensor; MDL: minimum detection limit of the sensor; Ref.: reference; —: not reported; HKUST-1: MOF copper(II) benzene-1,3,5-tricarboxylate.

Table 4 Summary of the advantages and disadvantages of each kind of material for chemiresistive H<sub>2</sub> sensors

Material	Advantages	Disadvantages
Pd-based	High selectivity Operating at room temperature	Poor long-term stability to high concentrations of H <sub>2</sub> Long response/recovery time High cost
MOS-based	High sensitivity Low detection limit Rapid response/recovery time	High operating temperature Poor selectivity Susceptible to humidity
Graphene	Operating at room temperature Large specific surface area High carrier mobility	Poor selectivity Long response/recovery time Low sensitivity
CNTs	Operating at room temperature High conductivity High surface-to-volume ratio	Poor reproducibility Low selectivity
TMDs	Operating at room temperature Tunable band gap	Poor selectivity Long response/recovery time
MXene	Operating at room temperature Large specific surface area	Poor sensitivity to low concentrations of H <sub>2</sub> Susceptible to humidity and oxygen

materials is highly efficient at room temperature; however, certain challenges persist. Graphene and CNTs exhibit low selectivity towards polar molecules and poor reproducibility. TMD-based H<sub>2</sub> sensors demonstrate prolonged response/recovery times, susceptibility to oxygen interference in ambient air, and high reactivity towards polar gases. Additionally, MXenes display inadequate sensing performance for low concentrations of H<sub>2</sub>.

## 5. Conclusion and outlook

With the widespread application of hydrogen energy sources in various fields, there is a growing demand for high-performance chemiresistive H<sub>2</sub> sensors. In this review, we present a comprehensive overview of the recent advancements in chemiresistive H<sub>2</sub> sensors and provide a summary of the strategies employed for enhancing performance. For Pd-based sensors, the suppression of the phase transition and improvement in selectivity can be achieved through various approaches, encompassing nanostructure construction, device optimization, bimetallic formation, and integration with other materials. In the case of MOS-based sensors, enhancement of performance and reduction in operating temperature are attained *via* nanostructure design, surface modification, doping, and heterostructure construction. Regarding materials like graphene, CNTs, TMDs, and MXenes that are not inherently sensitive to H<sub>2</sub> themselves; their H<sub>2</sub> sensing primarily relies on the incorporation of Pd. In conclusion, we primarily discuss their enhancement mechanisms based on some representative research achievements in recent years.

Table 4 summarizes the advantages and disadvantages of each material. Despite significant advancements in the research of resistive H<sub>2</sub> sensors, there still exist certain challenges that necessitate further enhancements:

(1) Accurate measurement in different environments: the response signals of most sensors can be influenced by temperature and humidity, thereby constraining the reliability of practical applications for H<sub>2</sub> sensors. Furthermore, it is imperative to mitigate the influence of interfering gases in practical applications to achieve precise detection of the target gas. Hence, it is necessary to avoid cross-response and prevent false alarms.

(2) Achieving room temperature detection: most MOS-based H<sub>2</sub> sensors still operate at elevated temperatures, which not only improves their power consumption but also shortens their lifespan. Therefore, achieving room temperature operation is of great significance in reducing costs and improving safety in practical applications.

(3) Improving long-term stability: the poor long-term stability remains a significant challenge for most sensors in practical applications, particularly for Pd-based sensors, where achieving linear detection of high concentration H<sub>2</sub> while maintaining exceptional long-term stability proves to be arduous.

(4) Exploring novel materials: currently, the development based on Pd and MOS has gradually reached a state of maturity. Hence, it holds immense significance to explore novel materials capable of attaining heightened sensitivity, rapid response, superior selectivity, excellent humidity resistance, and operation at room temperature.

(5) Integration and miniaturization: with the advancement of the Internet of Things, the application scenarios for hydrogen gas sensors are progressively expanding. The integration of multiple functionalities into a compact sensor facilitates meeting diverse requirements across various scenarios.

## Author contributions

Yao Yang Liu: writing original draft, collecting references. Zhong Li: writing review & editing, supervision, funding acquisition. Yi Liang: writing review & editing. Tao Tang: writing review & editing. Jing Hao Zhuang: collecting references. Wen Ji Zhang: collecting references. Bao Yue Zhang: writing review & editing. Jian Zhen Ou: writing review & editing, project administration, supervision.

## Data availability

No primary research results, software or code and no new data were generated or analyzed as part of this review.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

This work was supported by the National Natural Science Foundation of China (521721155), the Sichuan Science and Technology Program (2024ZYD0010), the Opening Project of Jiangsu Key Laboratory of Advanced Structural Materials and Application Technology (ASMA202201), and the Fundamental Research Funds for the Central Universities (2682024ZTPY053). We would like to acknowledge Analytical and Testing Centre of Southwest Jiaotong University for field emission transmission microscope JEM-2100F.

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