

## REVIEW

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## Recent advances in 2D/nanostructured metal sulfide-based gas sensors: mechanisms, applications, and perspectives

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2D and nanostructured metal sulfide materials are promising in the advancement of several gas sensing applications due to the abundant choice of materials with easily tunable electronic, optical, physical, and chemical properties. These applications are particularly attractive for gas sensing in environmental monitoring and breath analysis. This review gives a systematic description of various gas sensors based on 2D and nanostructured metal sulfide materials. Firstly, the crystal structures of metal sulfides are introduced. Secondly, the gas sensing mechanisms of different metal sulfides based on density functional theory analysis are summarised. Various gas-sensing concepts of metal sulfide-based devices, including chemiresistors, functionalized metal sulfides, Schottky junctions, heterojunctions, field-effect transistors, and optical and surface acoustic wave sensors, are compared and presented. It then discusses the extensive applications of metal sulfide-based sensors for different gas molecules, including volatile organic compounds (*i.e.*, acetone, benzene, methane, formaldehyde, ethanol, and liquefied petroleum gas) and inorganic gas (*i.e.*, CO<sub>2</sub>, O<sub>2</sub>, NH<sub>3</sub>, H<sub>2</sub>S, SO<sub>2</sub>, NO<sub>x</sub>, CH<sub>4</sub>, H<sub>2</sub>, and humidity). Finally, a strengths–weaknesses–opportunities–threats (SWOT) analysis is proposed for future development and commercialization in this field.

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## 1. Introduction

Nanostructured materials have been considered promising candidates for gas sensing applications due to their large surface area, abundant surface-active sites, and high surface reactivity.<sup>1</sup> They are primarily used for monitoring air quality, the environmental situation, and breath. Typically, atmospheric pollutants include nitrogen dioxide (NO<sub>2</sub>), nitrogen monoxide (NO), ammonia (NH<sub>3</sub>), hydrogen sulfide (H<sub>2</sub>S), sulfur dioxide (SO<sub>2</sub>), carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>), and volatile organic compounds (VOCs).<sup>2</sup> When these pollutants exceed the recommended exposure limits, they have negative effects on the environment and human health (Table 1). Therefore, the gas sensor needs to detect different gases simultaneously with high sensitivity and selectivity, a small size, low cost, and low power consumption (<10 mW).<sup>3</sup> In the aspect of breath analysis, different biomarkers from exhaled breath

need to be recognized accurately.<sup>4</sup> Normally, human breath contains nitrogen (N<sub>2</sub>), oxygen (O<sub>2</sub>), CO<sub>2</sub>, hydrogen (H<sub>2</sub>), inert gases, and water vapour. Sometimes, it includes organic VOCs *viz.* acetone, ethanol, isoprene, ethane, methane, pentane, *etc.*, and inorganic gases such as NO<sub>x</sub>, NH<sub>3</sub>, CO<sub>x</sub>, and H<sub>2</sub>S, see Fig. 1a. These excretory products diffuse into the inhaled air in the alveoli of the lungs and are then ejected in the form of exhaled air. Therefore, exhaled air carries different biomarkers, which can be used as fingerprints of metabolic products. This enables early diagnosis and prevention of respiratory diseases such as lung cancer, diseases of the kidneys, prostate, and bladder, and even Parkinson's disease, see Fig. 1b.<sup>5,6</sup> However, the maximum permissible limits of biomarkers are mostly at the parts-per-billion (ppb) level, which requires a highly sensitive gas sensor with a low limit of detection (LOD).

Solid-state sensors such as metal oxide semiconductors (MOSs),<sup>9</sup> carbon-based nanomaterials (CNMs),<sup>10–12</sup> and metal sulfide semiconductors<sup>13</sup> are used extensively in gas detection research. After Taguchi patented the first oxide-based gas sensor in 1962, various high sensitivity and low-cost gas sensors based on MOSs have been developed.<sup>14</sup> Tungsten oxide (WO<sub>3</sub>) nanotubes have been proved as a potential MOS for the detection of NO at the ppb level.<sup>15</sup> Orthorhombic molybdenum trioxide (α-MoO<sub>3</sub>) nanoribbons can detect NH<sub>3</sub> down to 280 ppt.<sup>16</sup> Gas sensors based on Pt functionalized tin dioxide (SnO<sub>2</sub>)<sup>17</sup> or indium oxide (In<sub>2</sub>O<sub>3</sub>)<sup>18</sup> can detect the lowest acetone

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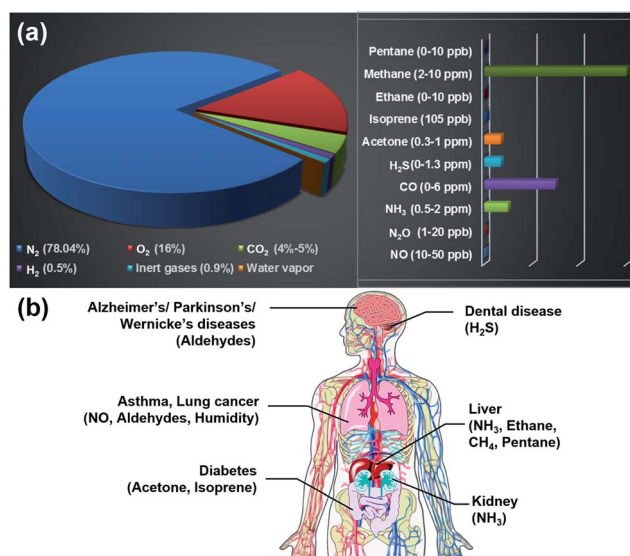
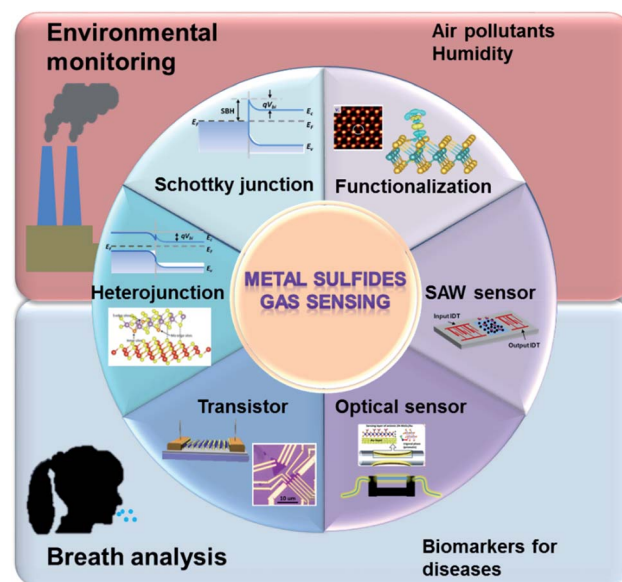
**Table 1** The environmental and human health impacts of different air pollutants and their maximum permissible limits set by the European Union<sup>7,8</sup>

| Gas              | Environmental and human health impact                                                                          | Maximum permissible limit |                          | Value of interest (ppb) |
|------------------|----------------------------------------------------------------------------------------------------------------|---------------------------|--------------------------|-------------------------|
|                  |                                                                                                                | 8 hours (ppm)             | Short-term (15 min, ppm) |                         |
| NO <sub>2</sub>  | Indirect green house gas, acidification, eutrophication, cardiovascular mortality, asthma, lung function       | 0.5                       | 1                        | 21                      |
| NH <sub>3</sub>  | Toxic, PM <sub>2.5</sub> precursor                                                                             | 20                        | 50                       | 20 000                  |
| H <sub>2</sub> S | SO <sub>2</sub> precursor, toxic                                                                               | 5                         | 10                       | 5000                    |
| SO <sub>2</sub>  | Indirect green house gas, acidification, particulate matter, precursor, cardiovascular mortality               | 0.5                       | 1                        | 7.5                     |
| CO               | Indirect green house gas, toxic, asthma, cardiovascular disease, cardiac disease, psychiatric admissions, etc. | 20                        | 100                      | 4000                    |
| CO <sub>2</sub>  | Green house gas – climate change                                                                               | 5000                      | —                        | 400 000                 |
| CH <sub>4</sub>  | Green house gas – climate change                                                                               | 1000                      | —                        | 1800                    |

concentration of 10 ppb. The ZnSnO<sub>3</sub> gas sensor can detect 100 ppb ethanol.<sup>19</sup> Many MOS-based devices can detect H<sub>2</sub>S at less than 1 ppm, such as copper oxide (CuO), SnO<sub>2</sub>, In<sub>2</sub>O<sub>3</sub>, zinc oxide (ZnO), titanium oxide (TiO<sub>2</sub>), and iron oxide (Fe<sub>2</sub>O<sub>3</sub>).<sup>20</sup> However, the operating temperature (OT) of MOS-based devices is usually high (100–300 °C), which induces high power consumption and consequently hinders the gas-sensing applications. CNMs, such as graphene and its derivatives and carbon nanotubes (CNTs), were employed as chemical gas sensors owing to their outstanding characteristics of a mesoporous nature, a large specific surface area, and enhanced electron transport properties.<sup>21</sup> Pristine reduced graphene oxide (rGO) can detect NH<sub>3</sub> and NO<sub>x</sub>, and rGO with a functionally modified surface (such as rGO/ZnO, rGO/Pt, and rGO/Ni) are known to detect VOCs (such as acetone, phenol, and nitrobenzene).<sup>22–24</sup> Rigoni *et al.*<sup>25</sup> recently demonstrated an NH<sub>3</sub> sensor comprising pristine SWCNTs that had a LOD of 3 ppb. The review of

graphene-based<sup>26</sup> and CNT-based<sup>12</sup> chemical sensors reported that 2D/nano-materials have great potential applications in gas detection and proposed several techniques to improve gas-sensing performance, which can be extended to other materials, for instance, metal sulfides.

Lots of metal sulfide-based sensors can work at room temperature and have lower power consumption, making them superior to MOS-based sensors.<sup>27</sup> The sensing performances of metal sulfides are similar to those of CNM-based devices, except for their sizeable and tunable bandgaps, making such materials suitable for transistor applications, further inducing unique

**Fig. 1** (a) The gas contents of human breath and (b) the biomarkers of different diseases.**Fig. 2** Strategies of high-performance metal sulfide-based gas sensors and their applications. The heterojunction image is reprinted with permission from ref. 35 Copyright 2017, ACS Publishing. The functionalization images are reprinted with permission from ref. 36. Copyright 2013, ACS Publishing and reprinted with permission from ref. 37. Copyright 2017, Elsevier. The transistor image is reprinted with permission from ref. 38. Copyright 2013, ACS Publishing. The optical sensor image is reprinted with permission from ref. 39. Copyright 2020, ACS Publishing.

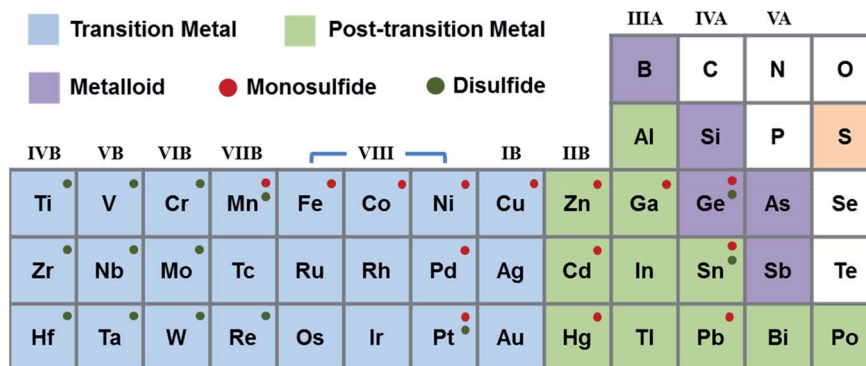


Fig. 3 Periodic table with symbols indicating metal sulfide.

sensing behaviours.<sup>28</sup> They have the advantages of a shallow valence band, exposed active sites, and the quantum size effect. Typical metal sulfide semiconductors, such as molybdenum disulfide (MoS<sub>2</sub>) and tungsten disulfide (WS<sub>2</sub>), are layered metal disulfide materials, which consist of several S-metal-S layers attached *via* weak van der Waals (vdW) force. Sensor metal sulfide materials act as charge acceptors or donors. Because of the high-speed charge transfer and the high adsorption energy between it and gas molecules, metal disulfide has been widely used in gas sensing. The LOD of a MoS<sub>2</sub> NO<sub>2</sub> gas sensor is 20 ppb.<sup>29</sup> For post-transition metal sulfide, tin sulfide (SnS) and germanium sulfide (GeS) are semiconductors that belong to a family of layered group IV monosulfides and have similar puckered structures to black phosphorus (BP).<sup>30–32</sup> Owing to its anisotropic crystal structure, SnS has been employed for the detection of VOCs and toxic gases, such as acetone, alcohol, and NO<sub>2</sub>.<sup>33,34</sup> Additionally, many advanced methods were proposed to improve their sensing properties, such as functionalizing metal sulfide (*e.g.*, with defects or dopants), constructing heterojunctions (Schottky junctions and p-n, n-n, and p-p heterojunctions), and using transistors, see Fig. 2.

The present review will provide a comprehensive perspective on metal sulfide-based gas sensors, including the crystal structure, gas sensing mechanisms, applications, and perspectives. The paper is organized as follows: Section 2 describes the basic characteristics of metal sulfide nanomaterials. Section 3 discusses various gas sensing mechanisms of different metal sulfides through density functional theory (DFT). Section 4 summarises different sensing concepts of gas sensors based on metal sulfides. Section 5 lists the gas sensing applications of metal sulfide-based devices. Section 6 discusses the challenges and perspectives of metal sulfide sensors. This review is conceptually self-contained and intended to serve as an informational resource to newcomers and experienced researchers on metal sulfide-based sensors.

## 2. Gas sensing mechanisms of metal sulfides

Sulfide is an inorganic sulfur anion with the chemical formula  $\text{S}^{2-}$  or a compound containing one or more  $\text{S}^{2-}$  ions.<sup>40</sup> Metal sulfide is a kind of combination of sulfur anions and metal/

semi-metal cations in the form of  $M_xS_y$  ( $x:y = 1:1, 1:2, 2:1, 3:4$ ).<sup>41</sup> As shown in Fig. 3, metal monosulfides mostly correspond to group VIII, IB, IIB, IIIA, and IVA metals. The elements from group IVB–VIIB and Sn can be used to form metal disulfides.<sup>42</sup> Materials of the same composition with different crystal phases have different properties. 2H phase group VIB disulfides are usually semiconducting, while the corresponding 1T, 1T', and Td phase crystals are metallic. Group IVA disulfides, such as  $GeS_2$  and  $SnS_2$ , are often semiconductors.  $MoS_2$ ,  $WS_2$ , and  $SnS_2$  are group VIB semiconductors, which have been used for transistors. Compared to other disulfides, group IVB disulfides exhibit high carrier mobility. Table 2 introduces the characteristics and applications of nanostructured metal sulfides. It is found that numerous metal sulfides possess several crystal phases, which can be controlled by altering the fabrication processes and external stimulations.<sup>41,43,44</sup> The preparation strategies for metal sulfides primarily comprise “top-down” and “bottom-up” methods. The top-down approaches include sputtering, electrospinning, lithography, mechanical exfoliation (ME), and liquid phase exfoliation (LPE). Bottom-up strategies are chemical vapour deposition (CVD), atomic layer deposition (ALD), spray pyrolysis, pulsed laser deposition/ablation, thermal deposition, hydrothermal synthesis, solvothermal synthesis, and the self-assembly method. All these methods have been proposed to prepare large scale, high yield, and low-cost metal sulfides in the form of 0D, 1D, 2D, and 3D structures. Chandrasekaran *et al.*<sup>40</sup> presented a comprehensive review on preparation technologies of metal sulfides; complementarily, in this review we primarily focus on gas sensing mechanisms and applications.

It is demonstrated that the gas molecules physically or chemically adsorb at the surface of the nanostructured materials through adsorption energy. The higher the adsorption energy the stronger the adsorption interaction between gas molecules and metal sulfides. First-principles simulation, that is DFT calculations using plane waves and pseudopotentials, has become an efficient method to evaluate the sensing performance of 2D/nano-materials. Because the behaviours of atoms during chemical bonding and the flow of electrons in materials can be calculated through DFT based on quantum

Table 2 Characteristics and applications of nanostructured metal sulfides<sup>a</sup>

|                                | Crystal structure               | Electric conductivity            | Bandgap [eV]                                        | Fabrication method                 | Application                                                   | Ref.      |
|--------------------------------|---------------------------------|----------------------------------|-----------------------------------------------------|------------------------------------|---------------------------------------------------------------|-----------|
| SnS                            | Orthorhombic                    | p-type                           | Indirect 1.1                                        | PVD                                | Photodetectors, gas sensors                                   | 45        |
| GaS                            | Hexagonal                       | Semiconductor                    | Indirect 2.52                                       | LPE                                | Hydrogen evolution reaction                                   | 46        |
| GeS                            | Orthorhombic                    | p-type                           | (Monolayer) indirect 2.34                           | Vapour deposition                  | High electron mobility                                        | 32        |
| ZnS                            | Hexagonal                       | n-type                           | Direct 3.7                                          | Hydrothermal                       | Gas sensors, optical sensors                                  | 47        |
| CdS                            | Hexagonal                       | n-type                           | Direct 2.42                                         | Spray pyrolysis                    | Solar cells, gas sensors                                      | 48        |
| CuS                            | Hexagonal                       | p-type                           | Direct 2.5                                          | Deposition                         | Solar cells, gas sensors                                      | 49        |
| PbS                            | Hexagonal                       | n-type                           | Bulk 0.373 nm 1.30                                  | Chemical bath deposition           | Solar cells, photonics, gas sensors                           | 50 and 51 |
| NiS                            | Rhombohedral                    | p-type                           | 0.5                                                 | Solventless, thermal decomposition | Photocatalysts                                                | 52        |
| MoS <sub>2</sub>               | 2H hexagonal<br>1T              | (2H) semiconductor<br>(1T) metal | (Bulk) indirect 1.29<br>(Monolayer) direct 1.8      | CVD, ME                            | FETs, photodetectors, solar cells, photonics, supercapacitors | 53 and 54 |
| WS <sub>2</sub>                | 2H hexagonal<br>1T              | (2H) n-type<br>(1T) metal        | (Bulk) indirect 1.3<br>(Monolayer) direct 2.1       | CVD, ME                            | FETs, photodetectors, gas sensors                             | 55        |
| SnS <sub>2</sub>               | 4H hexagonal                    | n-type                           | (Bulk) indirect 2.308<br>(Monolayer) indirect 2.033 | CVD, ME                            | FETs, photovoltaics, photodetectors                           | 56        |
| ZrS <sub>2</sub>               | 1T rhombohedral                 | n-type                           | (Bulk) indirect 1.7                                 | CVD                                | Photoconductivity                                             | 57        |
| HfS <sub>2</sub>               | 1T rhombohedral                 | Semiconductor                    | Indirect 2.0                                        | ME                                 | FETs, phototransistors                                        | 58        |
| NbS <sub>2</sub>               | 2H hexagonal                    | Metal                            | 0.73                                                | CVD                                | Superconductivity                                             | 59        |
| TaS <sub>2</sub>               | 1T rhombohedral<br>2H hexagonal | Metal                            | 0.7                                                 | CVD                                | Photosensitivity, superconductivity                           | 60        |
| TiS <sub>3</sub>               | Monoclinic                      | n-type                           | Direct 1.13                                         | ME, CVT                            | Photodetectors, gas sensors                                   | 61 and 62 |
| ZrS <sub>3</sub>               | Monoclinic                      | n-type                           | Direct 2.56                                         | CVT                                | Photodetectors                                                | 63        |
| HfS <sub>3</sub>               | Monoclinic                      | Semiconductor                    | —                                                   | CVT                                | FETs, photodetectors                                          | 64        |
| TaS <sub>3</sub>               | Orthorhombic                    | Metal                            | —                                                   | —                                  | FETs, gas sensors                                             | 65        |
| In <sub>2</sub> S <sub>3</sub> | Tetragonal                      | n-type                           | Direct 2.02                                         | CVD                                | Photodetectors, gas sensors                                   | 66        |

<sup>a</sup> Physical vapour deposition (PVD), chemical vapour transport (CVT).

mechanics, it is much easier to understand the behaviour of systems at the atomic scale. This section discusses the major parameter calculated using DFT for evaluating sensing performance, the sensing mechanism of different metal sulfide materials, such as pristine, doped, defective, and heterojunction-based metal sulfides.

## 2.1 Performance parameters based on DFT results

First-principles calculations are performed to calculate the band structure, adsorption energy ( $E_a$ ), charge transfer ( $\Delta Q$ ), bandgap ( $E_g$ ), charge density difference (CDD), electron localization function (ELF), and density of states (DOS) of the gas molecule-metal sulfide system.

The  $E_a$  of gas molecules on a substrate can be calculated as,

$$E_a = E_{\text{bare system}} + E_{\text{gases}} - E_{\text{total system}} \quad (1)$$

where  $E_{\text{bare system}}$ ,  $E_{\text{gases}}$ , and  $E_{\text{total system}}$  are the total energies of the optimized bare metal sulfide, isolated gas molecules, and metal sulfide + gas molecule system, respectively. A negative value of  $E_a$  indicates that the adsorption is exothermic. The

higher the  $E_a$ , the stronger the interaction between gas molecules and metal sulfides;  $E_a$  has a great influence on the sensitivity/response of the chemiresistive gas sensor. Usually, the selectivity of materials can be determined through the  $E_a$  among different types of gases, because the higher the  $E_a$ , the higher the probability of adsorption towards the specific gas. As shown in Fig. 4, the  $E_a$  of the H<sub>2</sub>O/SnS system is relatively high (−0.388 eV) among the four types of gases in air, which indicates that SnS has good sensitivity and specificity for the detection of H<sub>2</sub>O in air.

In addition to  $E_a$ , the electron transport property changes should also be considered. Charge transfer ( $\Delta Q$ ) is the total charge in the adsorbed gas molecule. It is shown as charge difference after DFT calculation, which can be calculated as follows:

$$\Delta Q = Q_{\text{total system}} - Q_{\text{bare system}} - Q_{\text{gases}} \quad (2)$$

where  $Q_{\text{total system}}$ ,  $Q_{\text{bare system}}$ , and  $Q_{\text{gases}}$  are the total charge on metal sulfide + gases, metal sulfide, and gas molecules, respectively. The amount of charge transferred was calculated





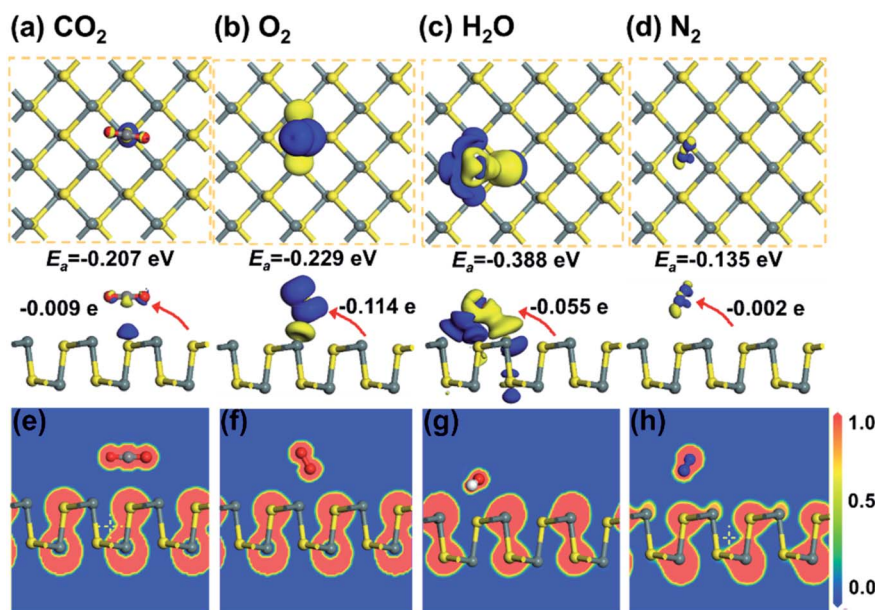


Fig. 4 The CDD for (a)  $\text{CO}_2$ , (b)  $\text{O}_2$ , (c)  $\text{H}_2\text{O}$ , and (d)  $\text{N}_2$  adsorbed on monolayer SnS. The isosurface is taken as  $0.003 \text{ e } \text{\AA}^{-3}$ . (e)–(h) show the corresponding ELF plots. Reprinted with permission from ref. 71. Copyright 2019, © IOP Publishing. All rights reserved.

by Löwdin analysis.<sup>67</sup> Some typical CDD images are shown in Fig. 4a–d. The blue region represents charge accumulation, while the yellow region shows charge depletion. These four types of gas molecule ( $\text{CO}_2$ ,  $\text{O}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{N}_2$ ) act as charge acceptors and receive electrons of  $0.009e$ ,  $0.114e$ ,  $0.055e$ , and  $0.002e$  from SnS, respectively.

In quantum chemistry, ELF is a measure of the possibility of finding an electron in the neighborhood space of a reference electron at a given point and with the same spin.<sup>68</sup> The ELF provides a method for mapping the electron pair probability in multielectronic systems and a description of electron delocalization in molecules and solids.<sup>69</sup> It can be used to analyze the extent of spatial localization of the reference electron and classify the chemical bond for almost all classes of compounds.<sup>70</sup> The ELF plots are normalized and present as

a jellium-like homogeneous electron. The normalized values of 1.00, 0.50, and 0.00 refer to fully localized electrons, fully delocalized electrons, and very low charge density, respectively. Some typical ELF images are shown in Fig. 4e–h. It is found that there is no remarkable electron sharing between gas molecules and SnS, which indicates that the chemical bond is unformed.

The DOS of a system presents the features of the electronic structure, such as the bandgap in insulators and the width of the valence band. It helps to qualitatively analyze the effects of external stimulations on the electronic structure, such as molecules, pressure, mechanical strain, and electric field. Fig. 5a shows the total DOS of the adsorption system of SnS without and with  $\text{NH}_3$ . The DOS of the SnS system changes slightly after adsorbing  $\text{NH}_3$  molecules, which is associated with the electronic level

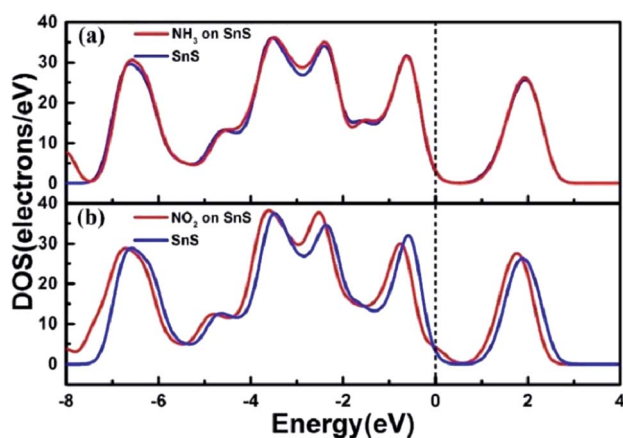


Fig. 5 The total DOS for (a)  $\text{NH}_3$  and (b)  $\text{NO}_2$  adsorbed on monolayer SnS. The Fermi level is set as zero. Reprinted with permission from ref. 72. Copyright 2017, IEEE.

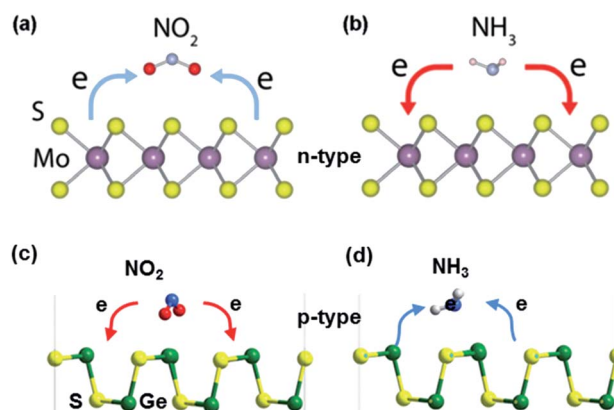
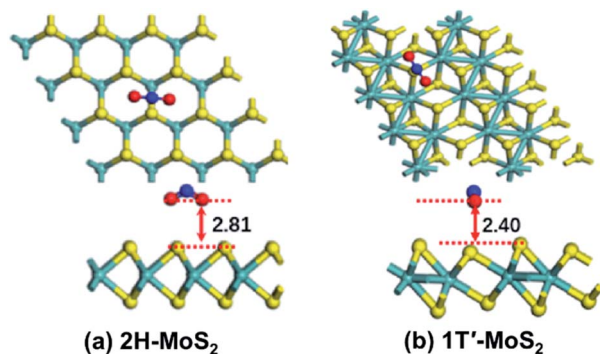


Fig. 6 Gas sensing mechanism of (a and b)  $\text{MoS}_2$  (n-type metal sulfide). Reprinted with permission from ref. 27. Copyright 2018, ACS Publishing. (c and d)  $\text{GeS}$  (p-type metal sulfide) in the presence of  $\text{NO}_2$  and  $\text{NH}_3$  molecules. Reprinted with permission from ref. 77. Copyright 2018, The Royal Society of Chemistry.



Adsorption Energies (eV) of Gas Molecules on Both 2H- and 1T'-MoS<sub>2</sub> Monolayers

| MoS <sub>2</sub> | CO    | CO <sub>2</sub> | NH <sub>3</sub> | SO <sub>2</sub> | NO    | NO <sub>2</sub> |
|------------------|-------|-----------------|-----------------|-----------------|-------|-----------------|
| 2H               | -0.14 | -0.31           | -0.18           | -0.30           | -0.16 | -0.21           |
| 1T'              | -0.15 | -0.22           | -0.22           | -0.35           | -0.47 | -0.25           |

Fig. 7 Top and side view of the most stable configurations of NO<sub>2</sub> molecules adsorbed on (a) 2H-MoS<sub>2</sub> and (b) 1T'-MoS<sub>2</sub>. The distance (Å) between the molecule (the lowest atom) and the MoS<sub>2</sub> sheets (the plane of the uppermost S atoms) is labelled. The bottom table shows the  $E_a$  of different gases on the 2H-MoS<sub>2</sub> and 1T'-MoS<sub>2</sub> monolayer. Reprinted with permission from ref. 79. Copyright 2019, ACS Publishing.

localized between  $-4$  eV and  $-2$  eV in the valence band. However, concerning the NO<sub>2</sub>/SnS system, there are obvious changes of the DOS on both sides near the Fermi level, which reveals the strong interaction between NO<sub>2</sub> and SnS (Fig. 5b).

## 2.2 Gas sensing mechanisms

### 2.2.1 Pristine metal sulfides

*N-type and p-type metal sulfides.* When exposed to gases, the charge transfer reaction occurs between the sensing materials and the adsorbed gases, accompanied by different transfer directions and quantities of charges, which leads to different

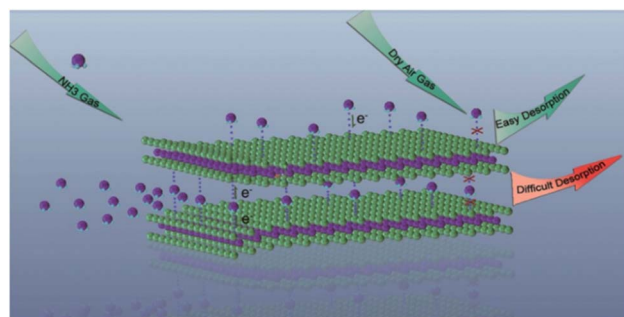


Fig. 9 The schematic of the interfacial interaction between the surface and interlayer of WS<sub>2</sub> and NH<sub>3</sub> molecules. Reprinted with permission from ref. 81. Copyright 2017, Elsevier.

changes in the material resistance. If the sensing materials are re-exposed to air, desorption of gas molecules occurs, causing the sensing material resistance to return to its initial state.<sup>73</sup> As shown in Fig. 6, when n-type MoS<sub>2</sub> is exposed to oxidizing gases such as O<sub>2</sub>, H<sub>2</sub>O, NO, NO<sub>2</sub>, and CO, the electron charges transfer from MoS<sub>2</sub> to the sensitive gases, leading to a decreased carrier density in MoS<sub>2</sub>. As a result, the resistance of n-type MoS<sub>2</sub> increases. In contrast, reducing (NH<sub>3</sub>) gas molecules adsorbed on MoS<sub>2</sub> act as charge donors and transfer electrons to the MoS<sub>2</sub> monolayer, increasing the electron carrier density of the n-type MoS<sub>2</sub> monolayer and reducing its resistance.<sup>74</sup> Among post-transition metal sulfides, GeS is a p-type semiconductor, where the electron-accepting gases act as charge donors to GeS and NH<sub>3</sub> molecules trap electrons from GeS. Besides, lots of DFT calculations proved that gas molecules adsorb more strongly at the edge sites than at the basal plane of metal sulfides.<sup>75,76</sup>

*2H and 1T' phase of metal sulfides.* 2H phase group VIB metal disulfides are usually semiconducting, and the corresponding

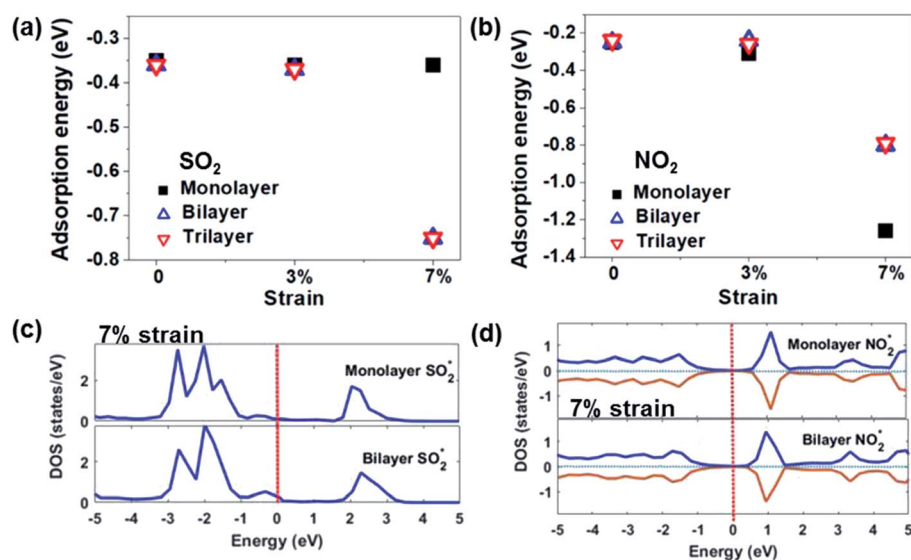


Fig. 8 Adsorption energies of (a) SO<sub>2</sub> and (b) NO<sub>2</sub> on 1T'-MoS<sub>2</sub> sheets with a different number of layers and different strains. Total DOS of MoS<sub>2</sub> monolayer and bilayer systems at 7% strain adsorbed by (c) SO<sub>2</sub> and (d) NO<sub>2</sub>. Reprinted with permission from ref. 79. Copyright 2019, ACS Publishing.

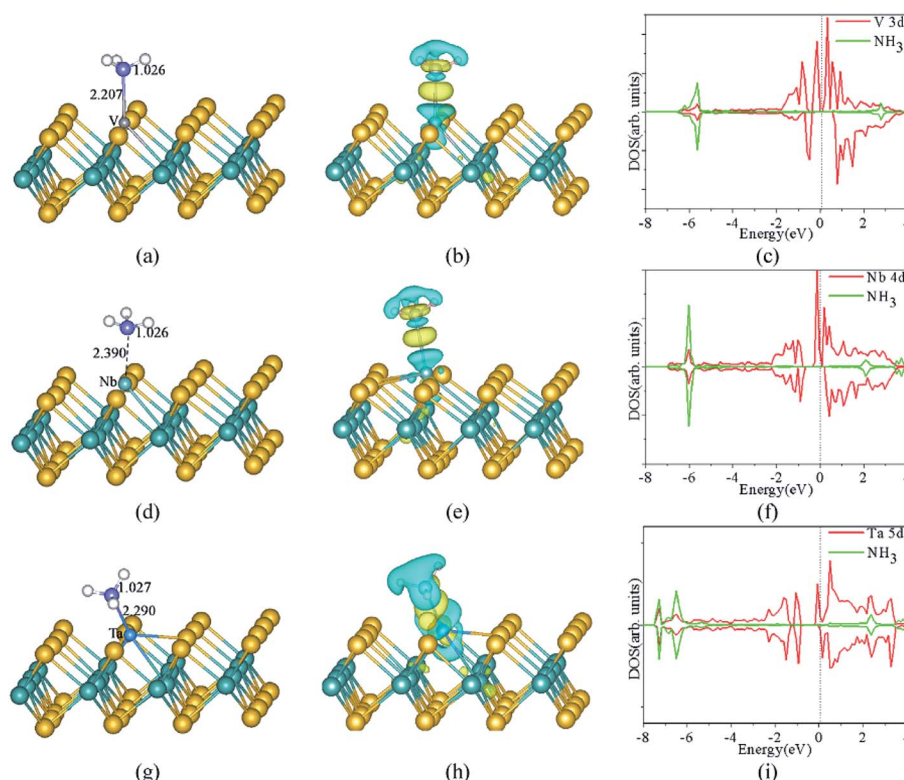


1T, 1T', and Td phase crystals are metallic. Different phases of metal sulfides have different  $E_a$  of the gas molecules over the sensor's surface. Putungan *et al.*<sup>78</sup> demonstrated that 1T'-MS<sub>2</sub> (M = Mo, W) are more stable than their 1T phases, ideal candidates for hydrogen evolution reaction (HER) catalysts. Linghu *et al.*<sup>79</sup> proved that the H adsorption strength on the basal plane of 1T'-MoS<sub>2</sub> is approximately 1.5 eV higher than that of 2H-MoS<sub>2</sub> because the molecules are closer to the 1T'-MoS<sub>2</sub> surface, allowing closer and stronger interaction. Besides, the 1T'-MoS<sub>2</sub>-based sensors have higher  $E_a$  towards gas molecules (*i.e.*, CO<sub>x</sub>, NH<sub>3</sub>, SO<sub>2</sub>, and NO<sub>x</sub>) than the sensors of 2H-MoS<sub>2</sub>. The table in Fig. 7 reveals that 1T'-MoS<sub>2</sub> has high sensitivity and selectivity toward NO gas molecules. Tang *et al.*<sup>80</sup> compared and analyzed the stability and band-gap state of the 2H phase and 1T phase MoS<sub>2</sub> by covalent functionalization with H, CH<sub>3</sub>, CF<sub>3</sub>, OCH<sub>3</sub>, and NH<sub>2</sub>. The results showed that the chemical bonding is strong in the 1T phase but very weak in the 2H phase, associated with the metallicity and partially filled Mo 4d states of 1T-MoS<sub>2</sub>.

**The effects of the number of layers.** It is well known that the number of layers affects the electronic properties of 2D materials. Based on the experimental results, it is found that multi-layer or few-layer MoS<sub>2</sub> was more stable and showed better gas sensing performance than its monolayer counterpart.<sup>82,83</sup> Concerning the DFT analysis results, Linghu *et al.*<sup>79</sup> investigated the

adsorption behaviour of SO<sub>2</sub>, NH<sub>3</sub>, NO, and NO<sub>2</sub> on bilayered and trilayered 1T'-MoS<sub>2</sub> sheets, as shown in Fig. 8. The 1T'-MoS<sub>2</sub> sheets with different thickness show only an approximately 0.01 eV change from the monolayer sheets without external mechanical strain. After applying 7% strain, the  $E_a$  of the trilayered system changes significantly compared to that of the monolayer systems. This is associated with the new hybridized states or the occupied states of the gases near the Fermi level. Furthermore, the number of layers influences the recovery time of the devices. Qin *et al.*<sup>81</sup> found that the recovery time after detecting NH<sub>3</sub> has an anti-linear relationship with the number of layers. According to their DFT calculation results, the  $E_a$  of the NH<sub>3</sub> molecule intercalated into the interlayer of WS<sub>2</sub> (−0.356 eV) is higher than that of surface desorption (−0.179 eV), as shown in Fig. 9. The ratio of intercalated NH<sub>3</sub> to surface-adsorbed NH<sub>3</sub> becomes larger as the layer number increases. Therefore, the more the layers of WS<sub>2</sub>, the longer the recovery time that is needed.

**2.2.2 Doped metal sulfides.** Chemical doping is an efficient way to change the band structure, modify the electronic and transport properties, and enhance the gas sensing applications. Metal doping is the most common method used for metal sulfides. Fig. 10 shows that typically doped metal atoms (*i.e.*, V, Nb, and Ta) replace the Mo atoms of metal sulfides. Table 3 lists the different types of metal dopants for monolayer MoS<sub>2</sub>, such



**Fig. 10** The optimized structures, CDD, and corresponding spin-polarized DOS projected on 3d states of V atoms, adsorbed gas molecules of NH<sub>3</sub> adsorbed on the monolayer MoS<sub>2</sub> with V (a, b and c), Nb (d, e and f), and Ta (g, h and i) doped in the S-vacancy, respectively. The Mo, S, N, H, V, Nb, and Ta atoms are denoted by dark green, yellow, purple, white, light grey, light green, and blue spheres, respectively. The yellow and cyan regions represent the positive (electron accumulation) and negative (electron depletion) values, respectively. The isosurface value is taken as 0.003 e Å<sup>−3</sup>. The vertical dashed line indicates the position of the Fermi level, taken as zero energy. Reprinted with permission from ref. 37. Copyright 2017, Elsevier.

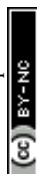




Table 3 Literature study on the  $E_a$  of doped metal sulfide nanomaterials with different gas molecules

| Material         | Type of doping                         | NO <sub>2</sub> | NO     | CO     | NH <sub>3</sub> | SO <sub>2</sub> | H <sub>2</sub> S | SF <sub>6</sub> | O <sub>2</sub> | H <sub>2</sub> | COF <sub>2</sub> | CF <sub>4</sub> | H <sub>2</sub> O | Ref. |
|------------------|----------------------------------------|-----------------|--------|--------|-----------------|-----------------|------------------|-----------------|----------------|----------------|------------------|-----------------|------------------|------|
| MoS <sub>2</sub> | Pristine                               | −0.069          | —      | —      | −0.063          | —               | —                | —               | —              | —              | —                | —               | —                | 85   |
|                  | Al-doped                               | −3.02           | —      | —      | −2.116          | —               | —                | —               | —              | —              | —                | —               | —                |      |
|                  | Si-doped                               | −2.588          | —      | —      | −2.156          | —               | —                | —               | —              | —              | —                | —               | —                | 86   |
|                  | P-doped                                | −2.134          | —      | —      | −0.34           | —               | —                | —               | —              | —              | —                | —               | —                |      |
|                  | Ni-doped                               | —               | —      | —      | —               | −1.382          | −1.319           | −0.181          | —              | —              | —                | —               | —                | 84   |
|                  | Ni-doped                               | —               | —      | —      | —               | —               | —                | —               | —              | —              | 0.723            | 0.265           | —                |      |
|                  | Pristine                               | —               | 0.11   | 0.07   | —               | —               | —                | —               | —              | —              | —                | —               | —                | 87   |
|                  | Cu-doped                               | —               | 1.25   | 1.44   | —               | —               | —                | —               | —              | —              | —                | —               | —                |      |
|                  | Au-doped                               | —               | 1.08   | 0.91   | —               | —               | —                | —               | —              | —              | —                | —               | —                | 88   |
|                  | Pt-doped                               | —               | 1.21   | 1.38   | —               | —               | —                | —               | —              | —              | —                | —               | —                |      |
|                  | Pd-doped                               | —               | 0.93   | 0.96   | —               | —               | —                | —               | —              | —              | —                | —               | —                | 37   |
|                  | Ni-doped                               | —               | 1.62   | 1.38   | —               | —               | —                | —               | —              | —              | —                | —               | —                |      |
|                  | V-doped                                | 3.08            | —      | 1.39   | 1.54            | —               | —                | —               | —              | —              | —                | —               | 1.12             | 37   |
|                  | Nb-doped                               | 4.30            | —      | 1.46   | 1.43            | —               | —                | —               | —              | —              | —                | —               | 0.99             |      |
|                  | Ta-doped                               | 4.05            | —      | 1.78   | 1.95            | —               | —                | —               | —              | —              | —                | —               | 1.65             | 89   |
|                  | Pristine                               | —               | —      | —      | —               | −0.36           | —                | —               | —              | —              | —                | —               | —                |      |
|                  | B-doped                                | —               | —      | —      | —               | −1.17           | —                | —               | —              | —              | —                | —               | —                | 90   |
|                  | N-doped                                | —               | —      | —      | —               | −0.58           | —                | —               | —              | —              | —                | —               | —                |      |
|                  | P-doped                                | —               | —      | —      | —               | −0.51           | —                | —               | —              | —              | —                | —               | —                | 91   |
|                  | Al-doped                               | —               | —      | —      | —               | −2.33           | —                | —               | —              | —              | —                | —               | —                |      |
|                  | Pristine                               | —               | —      | —      | —               | −0.209          | —                | —               | —              | —              | —                | —               | —                | 90   |
|                  | Ni-doped                               | —               | —      | —      | —               | −0.835          | —                | —               | —              | —              | —                | —               | —                |      |
|                  | Fe-doped                               | —               | —      | —      | —               | −0.218          | —                | —               | —              | —              | —                | —               | —                | 91   |
|                  | Co-doped                               | —               | —      | —      | —               | −0.213          | —                | —               | —              | —              | —                | —               | —                |      |
|                  | Au-doped                               | —               | —      | 1.16   | —               | —               | —                | —               | —              | —              | —                | —               | 0.41             | 91   |
|                  | Cu-doped                               | —               | —      | 1.31   | —               | —               | —                | —               | —              | —              | —                | —               | 0.68             |      |
|                  | AuCu-doped                             | —               | —      | 1.13   | —               | —               | —                | —               | —              | —              | —                | —               | 0.61             | 91   |
|                  | Au <sub>2</sub> Cu <sub>2</sub> -doped | —               | —      | 1.25   | —               | —               | —                | —               | —              | —              | —                | —               | 0.71             |      |
|                  | Au <sub>3</sub> Cu <sub>3</sub> -doped | —               | —      | 1.23   | —               | —               | —                | —               | —              | —              | —                | —               | 0.63             | 92   |
|                  | Pristine                               | —               | 0.25   | 0.21   | —               | —               | —                | —               | 0.22           | —              | —                | —               | 0.23             |      |
|                  |                                        | −0.354          | −0.206 | −0.127 | −0.216          | —               | —                | —               | −0.213         | −0.075         | —                | —               | −0.229           | 93   |

as Al, Si, P, Ni, Cu, Au, Pt, Pd, V, Nb, Ta, B, N, Fe, Co, and Au<sub>x</sub>Cu<sub>y</sub>, and their  $E_a$  after adsorbing different gas molecules (NO<sub>x</sub>, CO, NH<sub>3</sub>, SO<sub>2</sub>, H<sub>2</sub>S, SF<sub>6</sub>, O<sub>2</sub>, H<sub>2</sub>, carbonyl fluoride (COF<sub>2</sub>), cobalt tetrafluoride (CF<sub>4</sub>), and H<sub>2</sub>O). Based on the DFT results of all the metal-doped MoS<sub>2</sub> listed in Table 3, Ta-doped MoS<sub>2</sub> has the highest  $E_a$  of 4.30 eV towards NO<sub>2</sub>, 1.78 eV towards CO, and 1.65 eV towards H<sub>2</sub>O; Si-doped MoS<sub>2</sub> shows a high  $E_a$  of 2.156 eV to NH<sub>3</sub>; Al-doped MoS<sub>2</sub> shows an  $E_a$  of 2.33 to SO<sub>2</sub>. Besides, Li *et al.*<sup>84</sup> demonstrated that Ni-doped MoS<sub>2</sub> has great potential for sensing applications in organic gas molecules, such as COF<sub>2</sub> and CF<sub>4</sub>.

**2.2.3 Defective metal sulfides.** It is known that the MoS<sub>2</sub> monolayer exhibits naturally formed vacancies, such as S vacancies ( $V_S$ ) and Mo vacancies ( $V_{Mo}$ ), which have significant impacts on the gas sensing performance.<sup>94–97</sup> Zhao *et al.*<sup>94</sup> investigated various defects in monolayer MoS<sub>2</sub>, including monosulfur vacancies ( $V_S$ ), disulfur vacancies ( $V_{S_2}$ ), Mo vacancies ( $V_{Mo}$ ), a vacancy complex of Mo with three ( $V_{MoS_3}$ ) or six ( $V_{MoS_6}$ ) nearby sulfur vacancies, antisite defects where a Mo atom is substituting a sulfur atom ( $Mo_S$ ) or an S<sub>2</sub> column ( $Mo_{S_2}$ ), antisite defects where a sulfur atom ( $S_{Mo}$ ) or S<sub>2</sub> column ( $S_{2Mo}$ ) substitutes a Mo, and an external Mo ( $Mo-In$ ). They found that four types of defect systems were stable after geometry optimizations, as shown in Fig. 11. These are monosulfur vacancies ( $MoS_2-V_S$ ), disulfur vacancies ( $MoS_2-V_{S_2}$ ),

antisite defects ( $MoS_2-MoS$ ), and external Mo atoms ( $MoS_2-Mo$ ). The corresponding  $E_a$  values after adsorbing O<sub>2</sub> are −1.822, −1.687, −3.293, and −2.545 eV for  $MoS_2-V_S-O_2$ ,  $MoS_2-V_{S_2}-O_2$ ,  $MoS_2-MoS-O_2$ , and  $MoS_2-Mo-O_2$ , respectively. All of them are much stronger than that of pristine MoS<sub>2</sub> (−0.01 eV).

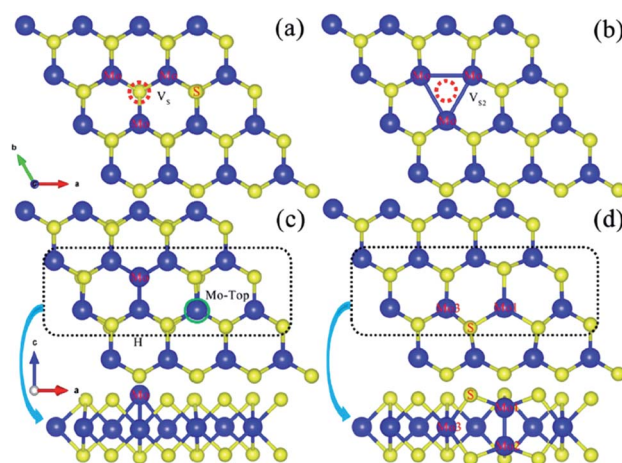


Fig. 11 Optimized geometric structure of the defect within a monolayer MoS<sub>2</sub>: (a) monosulfur vacancy ( $V_S$ ), (b) disulfur vacancy ( $V_{S_2}$ ), (c) antisite  $Mo_S$ , and (d) an external Mo located on the top of the Mo lattice site. Reprinted with permission from ref. 94. Copyright 2017, Elsevier.





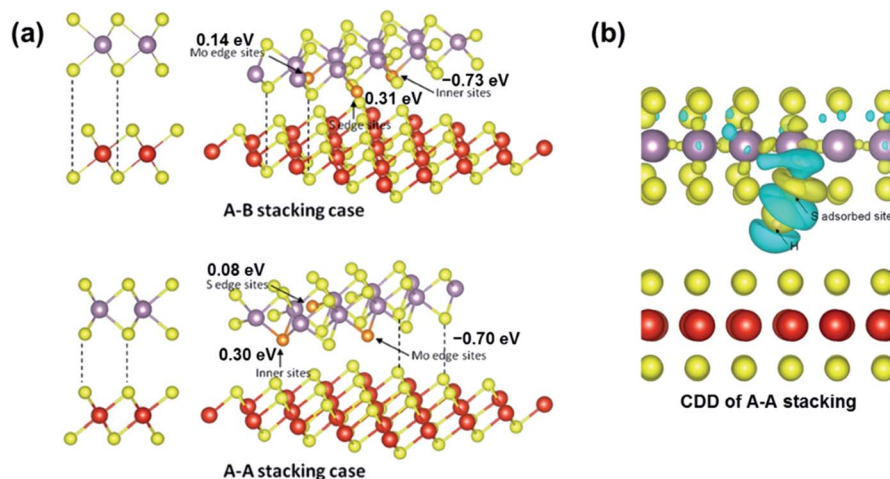


Fig. 12 (a) Two types of stacked bilayer structural models and their adsorption configurations. (b) CDD of the A-A stacking case (right) of the  $\text{VS}_2/\text{MoS}_2$ -edge nanosheet. The cyan and yellow regions represent the charge depletion and accumulation space, respectively. Reprinted with permission from ref. 35 Copyright 2017, ACS Publishing.

The CDD results reveal typical chemisorption of  $\text{O}_2$  on the defective surface, which is associated with the O-O bond length extension in varying degrees.

**2.2.4 Metal sulfide-based heterojunctions.** Different stacking methods affect the  $E_a$  of the gas/substrate system. As shown in Fig. 12a,  $\text{MoS}_2/\text{VS}_2$  heterojunctions with A-B and A-A stacking are built and used to investigate their hydrogen evolution ability.<sup>35</sup> The Gibbs free energies of the inner sites and Mo and S edge sites of the A-B and A-A stacking cases were also compared. The corresponding energies were calculated to be -0.73, 0.14, and 0.31 eV for the A-B stacking cases and -0.70, 0.08, and 0.30 eV for the A-A stacking cases. The difference of energies in these two stacking cases is associated with the bandgap barrier from  $\text{VS}_2$  to  $\text{MoS}_2$ , which induces different internal charge transfer. The CDD image in Fig. 12b further proves the charge transfer between the adjacent H atoms and the S atom. There is still a lack of DFT simulation results of the gas molecule/heterojunction system for metal sulfides. Lots of experimental results are analyzed based on bandgap theory, which will be described in the next section.

### 3. Various sensing concepts of metal sulfide-based devices

Based on the gas sensing mechanism, metal sulfide-based devices can be classified into chemiresistors, Schottky junctions, heterojunctions, field-effect transistors (FETs), and optical and surface acoustic wave (SAW) gas sensors. In this section, we introduce the performance parameters as well as the sensing concepts of these devices.

#### 3.1 Performance parameters

Typically, the criteria of an efficient gas sensor consist of high sensitivity and selectivity, fast response and recovery time, long-term stability, and low power consumption. Here, a set of parameters is defined to evaluate and compare the performance

of different sensors, including response, sensitivity, selectivity, LOD, dynamic range, response and recovery time, and stability.

**3.1.1 Response.** The response is defined as the change in measured current ( $I$ ), resistance ( $R$ ), capacitance ( $C$ ), conductance ( $G = I/V$ ), light power ( $P$ ), effective refractive index (RI), and resonant frequency ( $f$ ) for a given gas concentration unit concerning the signal in the absence of analyte molecules. It is defined as:

$$(X_{\text{gas}} - X_0)/X_0 = \Delta X/X_0 \quad (3)$$

where  $X = I, R, C, G, P, \text{RI}, \text{ or } f$ ,  $X_{\text{gas}}$  is the sensor's signal after adsorbing the analyte gas, and  $X_0$  is the baseline signal (no analyte gas). Different concentrations of the analyte gas could induce different responses. This review uses response in percentage ( $\text{response\%} = \text{response} \times 100\%$ ) to present the change of the testing signal.

**3.1.2 Sensitivity.** Sensitivity is defined as the capability to discriminate small differences in concentration or mass of the analyte. In other words, the sensitivity of the sensor is the slope of the calibration graph, which represents the variation in the sensor response per unit concentration of the target gas. In other words, sensitivity ( $S$ ) = response/concentration. Thus, a higher sensitivity indicates a higher efficiency of the sensor.

**3.1.3 Selectivity.** Selectivity refers to the strong adsorption of target gases in the mixed gas, while being insensitive to other gases. The selectivity factor/coefficient ( $K$ ) of the 'target gas' to another gas is defined as:

$$K = S_1/S_2 \quad (4)$$

where  $S_1$  and  $S_2$  are the sensitivities of the sensor to a target gas and another gas, respectively.

LOD is a key figure of merit in chemical sensing, used as an indicator of the minimum concentration of a detectable analyte.<sup>98</sup> Traditionally, LOD formulas, according to the International Union of Pure and Applied Chemistry (IUPAC), are based



on the use of linear regression models.<sup>98</sup> When the signal is three times greater than the noise, the theoretical LOD can be calculated from the slope of the linear region of the response curve, namely “Sensitivity (*S*)” and the root-mean-square (RMS) deviation at the baseline,

$$\text{LOD} = 3 \times \text{RMS}_{\text{noise}}/S \quad (5)$$

where  $\text{RMS}_{\text{noise}}$  is the noise level in the absence of the analyte gas. Concerning the LOD in non-linear gas sensors, including metal oxide sensors, gas FETs, or thermoelectric sensors, Burgués *et al.*<sup>99</sup> proposed a methodology to estimate LOD through linearized calibration models.

**Operating temperature (OT)** is the temperature that corresponds to maximum sensitivity.

**3.1.4 Response and recovery time.** The response time ( $\tau_s$ ) and recovery time ( $\tau_r$ ) are defined as the time required for reaching 90% of the final response and the time taken to recover 90% of the original value of the device. They are mostly used as an index of the speed of response, which is highly dependent on the types of gases, the device structure, and the exposure time.

**Stability** is defined as the ability of a sensor to provide consistent and reproducible results for a specified period. This parameter becomes highly important when sensors are exposed to hazardous, corrosive, or high-temperature atmospheres.

Usually, an ideal gas sensor would possess high sensitivity, selectivity and stability, low LOD, and short recovery and response times. But its final application depends on the requirements of the specified environment or working conditions. Moreover, all the parameters could be affected by other factors, including the sensing materials, substrate, environmental factors (temperature, humidity, and pressure), and testing setup (volume, shape, and gas flow rate).

### 3.2 Chemiresistor gas sensors

Typically, different types of metal sulfides, such as nanoflakes (NFKs), nanosheets (NSs), nanowires (NWs), nanorods (NRs), nanoflowers (NFWs), or nanotubes (NTs), are synthesized or transferred on a substrate (*i.e.*, sapphire, Si, and SiC) to form a chemiresistor sensor, as shown in Fig. 13. The electrodes can be pre-made on the substrate or evaporated on the top of metal sulfides after the transfer process.

As mentioned in Section 2.2, the basic sensing principle is metal sulfides act as charge acceptors or donors. Their shallow valence band, small effective mass, and diverse structures enable a quantum size effect and promising applications in gas

sensing. The typical direct narrow bandgap IV–VI compound semiconductors, such as SnS, PbS, and GeS, have similar puckered structures to black phosphorus.<sup>30,31</sup> They have been employed for the detection of toxic ( $\text{NO}_2$ ,  $\text{NH}_3$ , and  $\text{H}_2\text{S}$ ) and organic (*e.g.*, acetone and ethanol) gas molecules. The response and recovery time is fast (5–36 s).<sup>33,100,101</sup> The II–VI compound semiconductors mostly have a direct wide bandgap, including CdS and ZnS. They have high response and selectivity to VOCs, including isopropanol, methanol, ethanol, acetone, and methylbenzene. However, their OTs are relatively high (200–300 °C).<sup>102,103</sup> Other metal monosulfide-based gas sensors, such as CuS and NiS, also have potential applications in  $\text{H}_2$  and  $\text{SO}_2$  gas sensing.<sup>104–106</sup> According to Kim’s research, 75% of publications up to 2017 were focused on  $\text{MoS}_2$  followed by  $\text{WS}_2$  (14%) and  $\text{SnS}_2$  (9%).<sup>13</sup> The predominance of  $\text{MoS}_2$  over other metal disulfides is because this material is the easiest to synthesize and the most stable among transition metal sulfides. Most transition metal sulfides are composed of metal atoms sandwiched between two layers of hexagonally close-packed sulfur (S) atoms; the adjacent S layers are connected by the weak van der Waals forces. They have a larger electronegativity, potentially increasing the number of gas adsorption sites. Thus various transition metal sulfides, including  $\text{NbS}_2$ ,  $\text{ReS}_2$ ,  $\text{TaS}_2$ , and  $\text{VS}_2$ , were used for gas sensing in  $\text{NO}_x$ ,  $\text{NH}_3$ ,  $\text{O}_2$ , and ethanol.

Functionalization is a versatile method for the modulation of the electronic and chemical properties of metal sulfides. As discussed in Section 2.2, doping and defect substitution are the most commonly used tools in functionalization, which can change the electronic structure, modify chemical reactivity, and affect the sensing performance.<sup>108</sup> Fig. 14 shows a hydrogen sensor with few-layered Pd-doped  $\text{MoS}_2$  and various point defects in CVD- $\text{MoS}_2$ .<sup>36,107</sup> Qin *et al.*<sup>109</sup> demonstrated an enhanced  $\text{NH}_3$  sensor based on 2D  $\text{SnS}_2$  with sulfur vacancies. It showed a fast response time of 16 s toward 500 ppm  $\text{NH}_3$ . The enhanced sensitivity is associated with the high  $E_a$  of the defective system of 2D  $\text{SnS}_2$ . However, most of the gas-sensing behaviours of functionalized metal sulfides were analyzed through DFT calculations. There are a lack of experimental reports on the influence of defects on the metal sulfide-based devices’ gas-sensing performance.

### 3.3 Schottky junction

Typically, a metal–semiconductor (M–S) junction is a type of heterostructure where a metal is in close contact with a semiconductor material. The rectifying M–S junction is called a Schottky junction, while the non-rectifying junction forms an ohmic contact. Recently, researchers reported that a Schottky or an ohmic contact can also be formed between an atomic CNM and a semiconductor, depending on their electron affinity values.<sup>8</sup> Fig. 15a shows a typical Schottky junction, in which the electrons flow from the conduction band to the semiconductor layer until they reach equilibrium. This forms a Schottky barrier (SB) of the built-in potential barrier ( $V_{bi}$ ) in the contact layer and hinders further charge transport.<sup>110</sup> The Schottky barrier height (SBH) from the metal side remains unchanged, while the bias

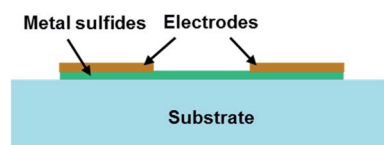


Fig. 13 Schematic of the structure of a metal sulfide-based chemiresistor gas sensor.



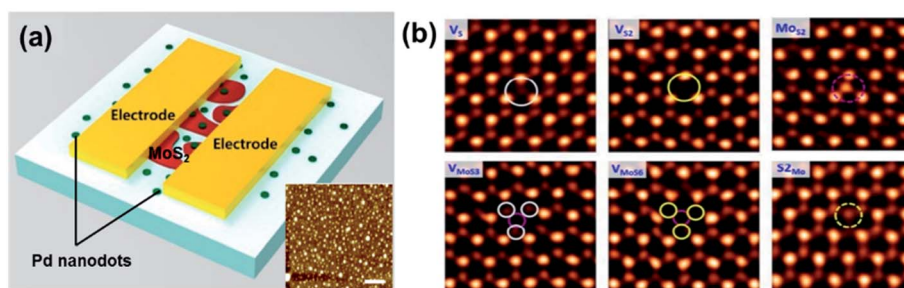


Fig. 14 (a) Schematic of a Pd-doped MoS<sub>2</sub>-based sensor. The inset image shows the AFM image of Pd on a SiO<sub>2</sub> substrate. The scale bars indicate a distance of 400 nm. Reprinted with permission from ref. 107. Copyright 2017, Elsevier. (b) Image analysis for intrinsic point defects in ML MoS<sub>2</sub>. Reprinted with permission from ref. 36. Copyright 2013, ACS Publishing.

across the junction could change according to the work function of the semiconductor ( $\phi_s$ ). As shown in Fig. 15b(i–v), the SBH was controlled using different metals (Au, Ag, and Al) as the materials of electrodes. The adsorbed gas molecules, *i.e.*, CO<sub>x</sub>, are a kind of dopant for the semiconductor, which could modify the doping level of materials and modulate the  $\phi_s$  in turn (see Fig. 15b(iv and v)).<sup>111</sup> The SB is determined from the difference between  $\phi_m$  and  $\phi_s$ , strongly influenced by the gas molecules. Therefore, the SBH is easily varied owing to the change of the gas concentration. Fig. 15b(ii) shows that the response to CO gas is improved in devices after using the Ag electrode due to the increase in SBH, which means that the Schottky contact sensor could improve the sensitivity because the modulations of the  $\phi_{B0}$  and barrier width in the Schottky junction by gas molecules are concentrated in the tiny area of contact between the metal and metal sulfides and the Schottky diode-based sensor can detect ultralow levels.<sup>112,113</sup> Besides, the sensing performances of vdW vertical heterojunctions of CNMs and

metal sulfides are not only associated with the SBH modulation mechanism but also with the abundant adsorption sites on the CNMs' surfaces. This enables a significant enhancement of the device sensitivity toward the ppb level of NO<sub>2</sub> gas exposure reaching 4.9%/ppb (4900%/ppm).<sup>114</sup>

### 3.4 Heterojunction based gas sensors

Heterojunctions based on metal sulfide can be easily constructed and present superior electric and photoelectric properties compared to pristine metal sulfide owing to the abundant adsorption sites and unique interface state at the contact interface.<sup>115</sup> According to the type of semiconductors, 2D heterojunctions can be classified as p–n, n–n, and p–p junctions.

**3.4.1 p–n junction.** The band alignment of a p–n heterojunction is shown in Fig. 16a; electrons and holes flow in opposite directions until equilibrium is achieved, forming a thick space-charge region that further narrows the electrical transport channels. Mostly, in p–n heterojunction gas sensors,

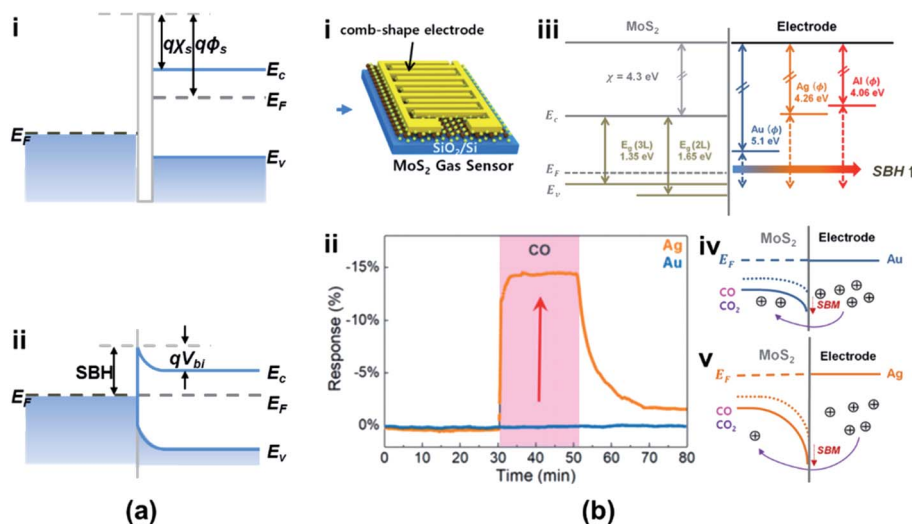


Fig. 15 Band alignment of (a) the Schottky junction.  $E_c$ ,  $E_F$ , and  $E_v$  are the conduction band edge, Fermi level, and valence band edge of the semiconductor, respectively.  $\phi_m$ ,  $\phi_s$ , and  $\chi_s$  are the metal work function (measured in volts), the semiconductor work function, and electron affinity, respectively.  $\phi_{B0}$ ,  $V_{bi}$ , and  $x_n$  are the barrier height, built-in potential barrier, and depletion width, respectively. Other symbols have their usual meaning. (b) (i) Schematic of the metal–MoS<sub>2</sub> Schottky contact gas sensor. (ii) Sensing characteristics of CO for 2 L MoS<sub>2</sub> with Au and Ag electrodes. (iii) Band diagram of MoS<sub>2</sub> with metal electrodes. Band alignment of (iv) the Au/MoS<sub>2</sub> gas sensor and (v) Ag/MoS<sub>2</sub> gas sensor before and after CO and CO<sub>2</sub> exposure. Reprinted with permission from ref. 111. Copyright 2019, ACS Publishing.

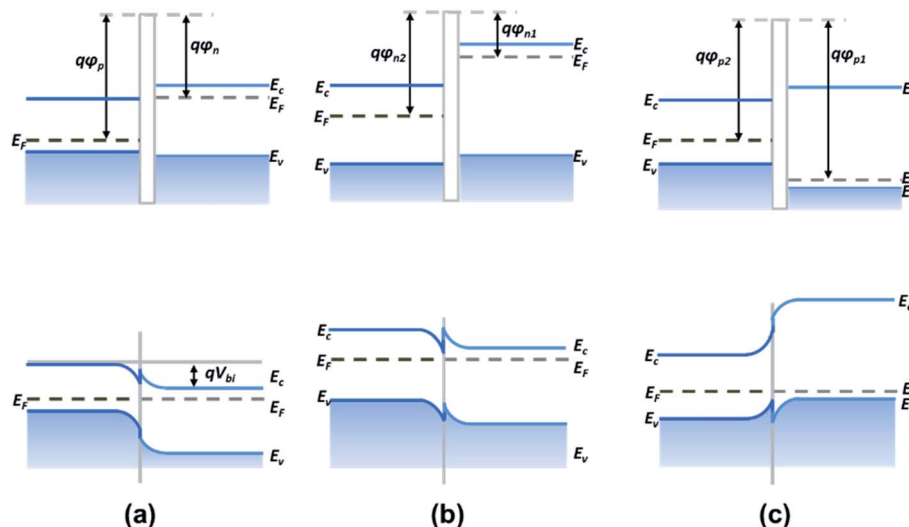


Fig. 16 Band alignment of (a) p–n junctions, (b) n–n junctions, and (c) p–p junctions.  $E_c$ ,  $E_f$ , and  $E_v$  are the conduction band edge, Fermi level, and valence band edge of the semiconductor, respectively.  $\phi_p$ ,  $\phi_n$ , and  $V_{bi}$  are the p-type semiconductor work function, the n-type semiconductor work function, and the built-in potential barrier, respectively.<sup>116</sup>

the sensing performances are determined by the difference in the areal coverage of the two dissimilar materials as well as the interfacial bonds.<sup>41,117</sup> With a higher areal coverage of the material, more electrons flow through the material, and so the charge transfer between gas molecules and the material is stronger than in the case of the material with lower areal coverage. Higher area materials dominate the sensing response of the p–n heterojunction. Concerning the interfacial states of a p–n junction, there are many dangling bonds and voids in the interface owing to a random connection between two different crystals.<sup>118</sup> Since dangling bonds could trap the electron in the conduction path, the charge transfer is impeded, requiring additional energy to drive the electrons across the electron-depletion layer (EDL). Therefore, it is recommended to keep the interface state at a low density, for instance, by adopting lattice-matched materials or enhancing the crystal quality of the materials. Through the hydrothermal method, MoS<sub>2</sub>/SnO<sub>2</sub> p–n heterojunctions have been fabricated and used for ethanol, trimethylamine (TMA), and NO<sub>2</sub> gas sensing.<sup>119–121</sup> They exhibited high sensitivity, lower OT, excellent sensing selectivity, and outstanding long-term stability. However, there are still a lack of quantitative experimental and theoretical analyses of the effects of areal coverage and dangling bonds on the gas sensing performances.

**3.4.2 n–n or p–p junction.** Recently, various n–n and p–p heterostructures have been proposed to improve the gas-sensing performances. Most of the n–n and p–p junction gas sensors are based on metal oxide nanomaterials, such as SnO<sub>2</sub>/TiO<sub>2</sub>,<sup>122</sup> SnO<sub>2</sub>/ZnO,<sup>123</sup> SnO<sub>2</sub>/Sn<sub>3</sub>O<sub>4</sub>,<sup>124</sup> TiO<sub>2</sub>/ZnO,<sup>125</sup> CaO/ZnO,<sup>126</sup> ZnO/In<sub>2</sub>O<sub>3</sub>,<sup>127</sup> and CuO/rGO,<sup>128</sup> whose enhanced performances are attributed to the heterocontact of the two semiconductor surfaces. For metal sulfide-based n–n and p–p heterojunctions, Zhang *et al.*<sup>129</sup> optimized the NH<sub>3</sub> sensing behaviour by using SnS<sub>2</sub>/ZnS hierarchical NFWs. The gas sensors based on metal sulfide n–n junctions benefiting from metal oxide hybrids, such

as CdS/CeO<sub>2</sub>,<sup>130</sup> CdS/ZnO,<sup>131</sup> ZnS/ZnO,<sup>132</sup> and ZnS/CuO,<sup>133</sup> have been employed for the detection of VOC toxic gases. The electrons flow across the heterojunction from the higher Fermi level to the lower one, which induces band bending and EDL formation at the interface. This improves the transfer efficiency of the interfacial charge and increases the adsorption of oxygen species. An EDL and electron-accumulation layer (EAL) are formed at n–n (Fig. 16b) and p–p (Fig. 16c) heterointerfaces. The adsorbed gases on the surface could further influence the width of the EDL/EAL by extracting/giving electrons from/to the conduction band of the semiconductors. Therefore, the conductivity of the device could be altered with the type and the concentration of analytes (gas molecules). Moreover, the interface states of n–n or p–p heterojunctions need further experimental and theoretical analysis.

### 3.5 FET gas sensors

FET gas sensors have attracted much research interest because of their sensitive detection and miniaturization.<sup>134,135</sup> Fig. 17 shows a typical FET gas sensor consisting of a sensing semiconductor as a channel material, a back gate layer, a dielectric layer, and source and drain electrodes on the two ends of the channel material. The conductance of the channel can be modulated by applying different bias voltages on the gate electrode through a thin dielectric layer.<sup>8</sup> The channel materials could be pristine or functionalized metal sulfides and metal sulfide-based heterojunctions. Similarly to the chemiresistor gas sensor, gas detection can be realized by measuring the change of the current between the source and drain ( $I_{ds}$ ) before and after exposure to target gases. The primary difference is that the gate voltage could alter the channel's charge carrier concentration by modulating the electric field across the dielectric layer. Consequently, the charge transfer between channel and target gases could be modified in the form of





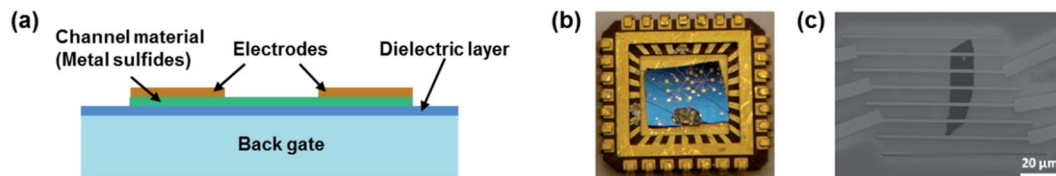


Fig. 17 (a) Schematic of an FET gas sensor. (b) Optical image of the MoS<sub>2</sub> transistor sensor on a chip. (c) SEM image of a two-layer MoS<sub>2</sub> transistor. Reprinted with permission from ref. 83. Copyright 2013, ACS Publishing.

changes in the  $I_{ds}$ . Traditionally, FET sensors could be back-gate FETs and top-gate FETs; however, most FET gas sensors are back-gate FETs because the channel materials can directly come into contact with target gases. This type of sensing device has been used to detect many types of gases, such as CO, NO, NH<sub>3</sub>, NO<sub>2</sub>, SO<sub>2</sub>, H<sub>2</sub>, and VOCs. However, most FET gas sensors are still not satisfactory due to their device instability and limited large-scale production even though they exhibit fast response and high selectivity.<sup>136</sup>

### 3.6 Optical gas sensors

Optical gas sensors monitor the optical properties of different gas species at defined optical wavelengths. They can be used as an optical “fingerprint” for any gas species because different types of gases have a specific distribution of optical absorption/emission with the wavelength. Besides, different changes in optical properties of sensors can reflect different gas concentrations. Metal sulfides have strong photoluminescence, a wide range of photoresponsivity, high carrier mobility, and high sensitivity to humidity variation.<sup>4,40</sup> Fibre-optic sensors are attractive due to their low cost, light weight, and anti-corrosion properties.<sup>137</sup> Therefore, taking advantage of the superior properties of both metal sulfides and optical fibres was considered. Most of metal sulfide-based optical gas sensors are fibre-optic devices. The MoS<sub>2</sub>-coated side polished fibre (SPF) sensor has a high response, and the MoS<sub>2</sub>-coated etched single-mode fibre (ESMF) has a fast response time, enabling the fibre-optic sensor to monitor different breathing patterns of human beings.<sup>138</sup> As shown in Fig. 18, the normalized response (NR) of the 2H-MoS<sub>2</sub>/Au coated optical fibre device was calculated from the change of the transmission light power, and the sensitivity

was determined using  $S = \Delta NR / \Delta RH$ , where  $\Delta NR$  is the relative variation in the transmitted light intensity for the sensor and  $\Delta RH$  is the change of relative humidity, respectively.<sup>39</sup>

### 3.7 SAW gas sensors

The SAW sensor is based on the microelectromechanical system (MEMS), which converts an input electrical signal into a SAW, i.e., a mechanical wave.<sup>139</sup> Fig. 19 shows a typical SAW gas sensor structure, whose SAW delay line between the input and output interdigital-transducer (IDT) is covered by a thin membrane that can selectively adsorb the gas to be detected. Any change in phase, frequency, amplitude, or time-delay induced by gas adsorption or desorption of the membrane, might further affect the wave. Then it is converted into an electrical signal and received by the output end. In particular, the phase velocities can be detected with high accuracy. In this case, SnS colloidal quantum dots (CQDs) were used as the sensing layer and fabricated on the ST-cut quartz substrate.<sup>140</sup> The sensor exhibited high selectivity and efficiency for the detection of NO<sub>2</sub> gas with low concentration at room temperature. Moreover, this is an efficient approach to diagnose diseases from exhaled breath by coating SAW sensors with various polymers to identify specific breath biomarkers.

## 4. Metal sulfide-based devices for gas sensing applications

### 4.1 VOCs

VOCs primarily come from the exhaust gases generated by transportation, fuel combustion, and come from cooking, furniture, decorative materials, or much simpler breathing.<sup>141</sup>

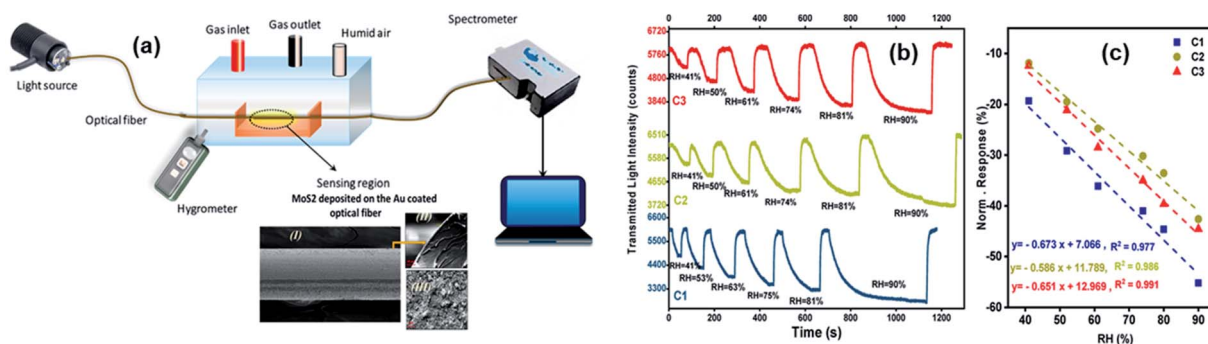


Fig. 18 (a) Schematic diagram of the gas sensing transmittance setup on the basis of an optical fiber coated with thin layers of anionic MoS<sub>2</sub> and Au. The inset image shows the cross-sectional FE-SEM images of the anionic 2H-MoS<sub>2</sub>/Au coated optical fibre. (b) Dynamic and (c) sensitivity responses of the optical fiber sensors modified with different samples. Reprinted with permission from ref. 39. Copyright 2020, ACS Publishing.



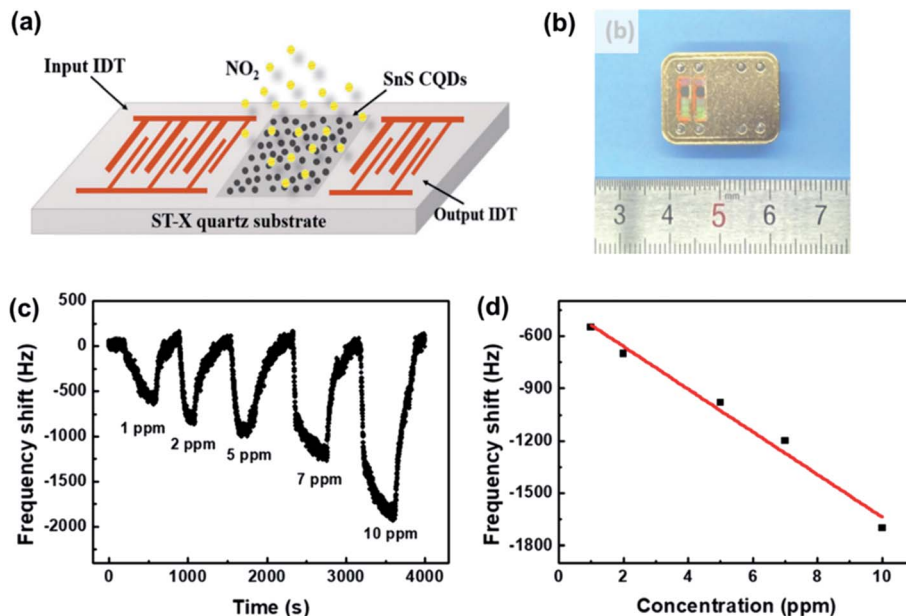


Fig. 19 (a) The schematic and (b) a photograph of the SAW sensor based on SnS CQDs. (c) The response curves of the SAW sensor to different  $\text{NO}_2$  concentrations. (d) The dependence of the response on  $\text{NO}_2$  concentration. Reprinted with permission from ref. 140. Copyright 2019, Elsevier.

Since the concentration of VOCs in an indoor ambient environment is much higher than that outdoors (up to 10 times), the level of VOCs is used as one of the indicators for evaluating the air quality in indoor ambient.<sup>98</sup> When people are exposed to a certain concentration of VOCs, they face a higher risk of suffering from headaches, nausea, and even organ damage. From a medical perspective, exhaled breath contains VOCs of alcohols, hydrocarbons, ketones, aldehydes, esters, nitriles, and aromatic compounds,<sup>142,143</sup> which can be used as biomarkers of the diagnosis of diseases according to Fig. 1. The gas-sensing performance of metal sulfide-based devices towards different VOCs is summarised in Tables 4–6.

**4.1.1 Acetone.** Acetone is one of the common metabolites of the human body and is ordinarily present in the breath, blood, and urine. Increased acetone in the breath can be found in untreated patients with diabetes mellitus.<sup>144,145</sup> Typically, the acetone concentration for diabetic patients is higher than 1.71 parts per million by volume (ppmv), whereas that for healthy people ranges from 0.3 to 0.9 ppmv.<sup>146</sup> The detection and analysis of acetone in the breath can be a potential method for the diagnosis of diabetes. Besides, acetone may also be associated with lung cancer.<sup>142</sup> To achieve high sensitivity, various shapes of metal sulfides were used. The SnS NFK-based gas sensor showed excellent stability and reproducibility at 100 °C for the detection of acetone from 5 to 50 ppm and a rapid response of 3 s.<sup>34</sup> Wang *et al.*<sup>103</sup> fabricated a single-crystal ZnS NW-based gas sensor through the thermal-evaporation-growth method, which showed high sensing selectivity towards acetone and ethanol. Giberti *et al.*<sup>147</sup> obtained  $\text{SnS}_2$  NRs as a precipitate in aqueous solution and deposited them as functional materials on an alumina substrate for acetone, acetaldehyde, and  $\text{H}_2\text{S}$  gas sensing. The sensor showed excellent

selectivity to acetone at 1 ppm under both dry and wet conditions at an OT of 300 °C. To decrease the OT,  $\text{SnS}_2/\text{SnO}_2$  heterojunctions were employed for the detection of acetone, and they showed a response% of 107% and fast recovery (80 s) at 80 °C.<sup>148</sup> However, the LOD could not meet the limit of acetone concentration in the exhaled breath (0.9 ppm), which shows that the LOD of metal sulfide-based gas sensors needs to be improved further.

**4.1.2 Benzene.** Benzene gas is volatile and highly toxic; even a small amount of benzene can cause vital harm to our body.<sup>149</sup> The maximum permitted exposure limit in the atmosphere regulated by the World Health Organization (WHO) is 5 ppb ( $16.25 \mu\text{g m}^{-3}$ ).<sup>150</sup> However, benzene is commonly used as a solvent in petrochemical and pharmaceutical goods, which has terrible carcinogenic effects on the people working there. It is necessary to detect trace benzene in the environment, which has led to the development of inexpensive sensors for benzene detection. The conventional methods are based on cataluminescence, chromatography, and spectroscopy.<sup>149,151,152</sup> Recently, semiconductor sensors were explored. For metal sulfide-based devices, Zhang *et al.*<sup>153</sup> synthesized and used Pd-decorated  $\text{TiO}_2/\text{MoS}_2$  ternary nanocomposites in the benzene sensor. Compared to pristine  $\text{MoS}_2$  and  $\text{TiO}_2$  sensors, this sensor has a higher response% of 64% for 50 ppm benzene, wider linearity ranging from 0.1 to 100 ppm, shorter response and recovery times (13 s/10 s), and better selectivity and stability. Moreover, this group employed  $\text{WS}_2$  NFWs/ $\text{ZnO}$  hollow spheres to detect benzene, which showed a faster response and recovery time of 8 s/6 s at room temperature.<sup>154</sup> To extend the application area, Baek *et al.*<sup>155</sup> demonstrated a flexible and transparent benzene sensor using cobalt-metalloporphyrin (Co-MPP)-functionalized few-layer  $\text{MoS}_2$  as the sensing material.



Table 4 Literature study on the gas-sensing performance of metal sulfide-based VOC gas sensors<sup>a</sup>

| Material                                                 | Structure          | Synthesis method                        | Analyte      | Concentration (ppm) | Response (%)                 | LOD (ppm) | $\tau_s/\tau_r$   | OT (°C) | Ref. |
|----------------------------------------------------------|--------------------|-----------------------------------------|--------------|---------------------|------------------------------|-----------|-------------------|---------|------|
| SnS                                                      | NFKs               | Solid state reaction                    | Acetone      | 20                  | 1000                         | —         | 3 s/14 s          | 100     | 34   |
| ZnS                                                      | NWs                | Thermal evaporation                     | Acetone      | 100                 | 2120                         | 0.5       | 10 s/7 s          | 320     | 103  |
| MoS <sub>2</sub>                                         | Nanofilm           | ME                                      | Acetone      | 5000                | ~1.2                         | 500       | —                 | RT      | 38   |
| SnS <sub>2</sub>                                         | NRs                | Precipitation in aqueous solution       | Acetone      | 10                  | ~2500 (dry)<br>~210 (17% RH) | 1         | —                 | 300     | 147  |
| Pd-TiO <sub>2</sub> /MoS <sub>2</sub>                    | Nanocomposites     | Hydrothermal method                     | Benzene      | 50                  | 64                           | 0.1       | 13 s/10 s         | RT      | 153  |
| ZnO/MoS <sub>2</sub>                                     | p-n junction       | Screen printing                         | Benzene      | 20                  | 30                           | 0.1       | 8 s/6 s           | RT      | 154  |
| Co-MPP-functionalized MoS <sub>2</sub>                   | Nanocomposites     | Solvent mixing                          | Benzene      | 10                  | 22                           | —         | ~500 s/<br>~100 s | RT      | 155  |
| PbS                                                      | NSs                | Chemical reaction                       | Methane      | 10 000              | ~10                          | —         | —                 | RT      | 159  |
| Au NPs/PbS                                               | Nanocomposites     | Chemical reaction                       | Methane      | 30 000              | 30                           | —         | 180 s/70 s        | RT      | 160  |
| Ag NPs/PbS                                               | Nanocomposites     | Chemical reaction                       | Methane      | 80 000              | 35                           | —         | 60 s/150 s        | RT      | 161  |
| PbS NCs/rGO                                              | Nanocomposites     | Chemical reaction & hydrothermal method | Methane      | 10 000              | 45                           | —         | 90 s/65 s         | RT      | 162  |
| ZnS:Mn <sup>2+</sup> (optical)                           | QDs                | Chemical precipitation                  | Methane      | 100                 | ~50*                         | —         | —                 | RT      | 164  |
| SnO <sub>2</sub> /MoS <sub>2</sub>                       | Nanocomposites     | Electrospinning and hydrothermal method | Methane      | 100                 | 101.4*                       | —         | 150 s/20 s        | 180     | 163  |
| ZnS                                                      | 0D nanosphere      | Hydrothermal method                     | Formaldehyde | 50                  | 9440*                        | —         | 11 s/8 s          | 295     | 165  |
| rGO/MoS <sub>2</sub>                                     | Hybrid films       | Layer-by-layer (LBL) self-assembly      | Formaldehyde | 10                  | 2.8                          | —         | —                 | RT      | 166  |
| In <sub>2</sub> O <sub>3</sub> /MoS <sub>2</sub>         | Nanocubes/nanofilm | LBL self-assembly                       | Formaldehyde | 50                  | 75.2                         | 0.2       | 14 s/22 s         | RT      | 167  |
| In <sub>2</sub> O <sub>3</sub> /WS <sub>2</sub>          | Nanocomposites     | LBL self-assembly                       | Formaldehyde | 5                   | 7.5                          | —         | 98 s/137 s        | RT      | 168  |
| Ni-doped In <sub>2</sub> O <sub>3</sub> /WS <sub>2</sub> | Nanocomposites     | LBL self-assembly                       | Formaldehyde | 20                  | 32                           | 0.015     | 76 s/123 s        | RT      |      |

<sup>a</sup> \* means the response% is recalculated as  $(X_{\text{gas}} - X_0)/X_0 = \Delta X/X_0$  in this review. In the original reference, the response (%) is defined as  $X_{\text{gas}}/X_{\text{air}}$ .

The device has a higher response% of over 250% compared to pristine MoS<sub>2</sub> and a low LOD of 10 ppm at room temperature.

**4.1.3 Methane.** Methane (CH<sub>4</sub>) is widely present in industrial and residential areas and emitted into the atmosphere from natural wetlands, rice paddies, domestic ruminants, landfills, and biomass burning.<sup>156</sup> It is a potent greenhouse gas, whose explosive limit concentration was reported to be more than 4.7% mixed with air.<sup>157</sup> Traditionally, exhaled air from normal human breath doesn't have methane, except in people who are overweight and people who have irritable bowel syndrome, inflammatory bowel diseases, or anorexia.<sup>158</sup> Taking advantage of the nanostructures, metal sulfide nanocrystals (NCs) and quantum dots (QDs) have been used in CH<sub>4</sub> sensors. Sheikhi *et al.* proposed a series of PbS-based chemiresistor sensors for the detection of CH<sub>4</sub>, including intrinsic PbS NCs,<sup>159</sup> Au nanoparticle (NP) decorated PbS,<sup>160</sup> Ag NP decorated PbS,<sup>161</sup> and PbS NCs/rGO hybrids.<sup>162</sup> The PbS NCs/rGO nanocomposite sensor has shown a good response% (45%) at the lower explosive limit of CH<sub>4</sub> with fast response and recovery time (90 s/65 s). Wang *et al.* employed hierarchical nanocomposites of MoS<sub>2</sub> NFWs anchored on SnO<sub>2</sub> nanofibers for CH<sub>4</sub> sensing. As shown in Fig. 20, this n-n junction-based sensor showed a high response% of 101.4% toward 100 ppm CH<sub>4</sub> at 180 °C.<sup>163</sup> With respect to optical gas sensors, Sergeev *et al.*<sup>164</sup> synthesized manganese-doped zinc sulfide (ZnS:Mn<sup>2+</sup>) QDs and found that the ZnS:Mn<sup>2+</sup> emission spectrum is changed significantly under exposure to CH<sub>4</sub> in the concentration range from 100 ppm to

2000 ppm. QDs in this luminescent sensor act as adsorption centres for achieving higher light transmittance and further improving the signal stability in the visible region. The response refers to the photoinduced electron transfer from QDs to CH<sub>4</sub>, which induces QD luminescence quenching and a decrease in the luminescence lifetime.

**4.1.4 Formaldehyde.** Formaldehyde (HCHO) is a colorless toxic gas with a pungent smell and can cause serious harm to the central nervous system and immune system of human beings. Because formaldehyde is a chemical used in the production of solvents, adhesives, and bonding agents, it is usually released from pressed-wood products, wallpapers, paints, and foam insulation in homes, offices, and the urban environment. According to the Occupational Safety and Health Standards, the time-weighted average limit of formaldehyde is 0.75 ppm, the short-term exposure limit is 2 ppm and the immediately dangerous to life or health limit is 20 ppm.<sup>169</sup> In the view of healthcare, HCHO could act as a biomarker of multiple diseases, especially lung cancer.<sup>150</sup>

Hussain *et al.*<sup>165</sup> successfully prepared 0D ZnS nanospheres via a low-temperature hydrothermal synthesis method. The gas sensor showed a high response% of 9540% and high selectivity towards formaldehyde compared to other gases (ethanol, ammonia, acetone, methanol, and NO<sub>2</sub>) at an OT of 295 °C. The enhanced gas-sensing performances can be attributed to the presence of more active sites because of the large exposed surface area and small size of ZnS nanospheres. Li *et al.*<sup>166</sup>



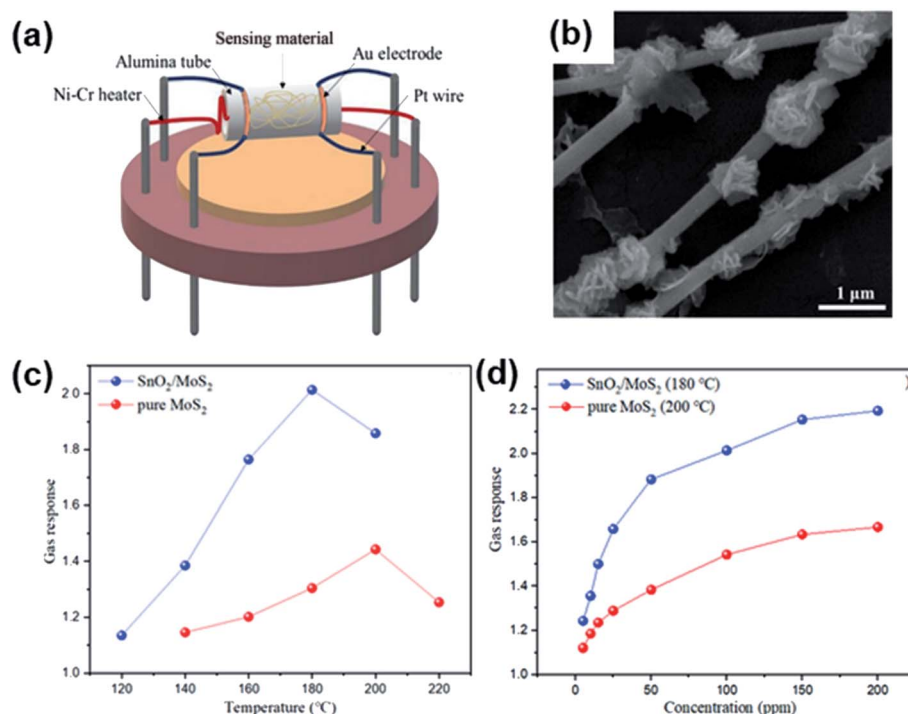


Fig. 20 (a) Schematic structure of a SnO<sub>2</sub>/MoS<sub>2</sub> gas sensor. (b) SEM results of SnO<sub>2</sub>/MoS<sub>2</sub> samples. (c) Gas response of sensor devices to 100 ppm CH<sub>4</sub> under different operating temperatures. (d) Gas response of two sensors to CH<sub>4</sub> with various concentrations. Reprinted with permission from ref. 163. Copyright 2019, Elsevier.

fabricated gas sensors based on rGO/MoS<sub>2</sub> hybrid films, which yielded flexible devices for formaldehyde detection at room temperature. The mechanisms for enhanced sensing performance of the rGO/MoS<sub>2</sub> hybrid films could be summarized as follows: in the hybrid film, MoS<sub>2</sub> nanosheets acted as the formaldehyde adsorbent and electron acceptor, mediating a two-stage electron transfer from formaldehyde and finally to rGO, which served as a conducting network and exhibited a p-type response. As shown in Fig. 21, Zhang *et al.* demonstrated some room temperature formaldehyde sensors based on a LBL self-assembled In<sub>2</sub>O<sub>3</sub> nanocubes/flower-like MoS<sub>2</sub> nanofilm,<sup>167</sup> and Ni-doped In<sub>2</sub>O<sub>3</sub>/WS<sub>2</sub> nanocomposite.<sup>168</sup> They exhibited a low LOD of 15 ppb, good selectivity, repeatability, fast detection rate, and a fair logarithmic function toward formaldehyde concentration. The dramatically enhanced sensing performance of the Ni-In<sub>2</sub>O<sub>3</sub>/WS<sub>2</sub> sensor can be attributed to the Ni ion doping and synergistic interfacial incorporation of the In<sub>2</sub>O<sub>3</sub>/WS<sub>2</sub> heterojunction.

**4.1.5 Ethanol.** Volatile alcohols such as ethanol are often found in the chemical, medical, pharmaceutical, and food industries. They can induce nasal and mucous membrane inflammation, respiration disruption, eyesight disturbance, nerve disease, lung irritation, and even death after long-term exposure to even a low alcohol vapour concentration. On the other hand, because ethanol is a kind of flammable gas, it is essential to monitor its real-time concentration in workplaces. Moreover, ethanol is one of the typical biomarkers for lung cancer. Thus it requires developing a high-performance gas sensor for the detection of low concentration ethanol.

Many pristine metal sulfides, such as SnS NFKs,<sup>34</sup> CdS thin films,<sup>171</sup> hollow sphere CuS,<sup>172</sup> and β-In<sub>2</sub>S<sub>3</sub> thin films,<sup>173</sup> were proposed for the detection of ethanol. At an OT of 300 °C, the CdS films show a high response% of 6300% and strong selectivity to alcohols in mixtures where aldehydes and other interferents are present. Their response and recovery time are speedy; however, their OTs are higher than 200 °C. Therefore, heterostructures of metal sulfides with metal oxides are introduced to enhance the sensing capability for alcohol detection. Both metal oxides and metal sulfide would have the same Fermi energy level at the interface, which results in a staggered band offset and a built-in internal electric field. When using the heterogeneous structure in a sensor, the electron generated from the adsorption reaction can easily move across the interface and transfer to the conductive band. In the context of metal sulfide/metal oxide heterostructures prepared through hydrothermal methods, MoS<sub>2</sub>/SnO<sub>2</sub>,<sup>119</sup> MoS<sub>2</sub>/ZnO,<sup>174</sup> and MoS<sub>2</sub>/TiO<sub>2</sub> (ref. 175) are three typical heterostructures. Among them, the MoS<sub>2</sub>/SnO<sub>2</sub> sensor showed an ultra-high response% of 11 900% toward 200 ppm ethanol. All of them have fast response and recovery time (~20 s); however, their OTs are higher than 150 °C. Thus a room-temperature ethanol sensor based on n-type α-Fe<sub>2</sub>O<sub>3</sub> hollow microspheres on MoS<sub>2</sub> NSs prepared by the LBL self-assembly method was proposed and is shown in Fig. 22.<sup>170</sup> The α-Fe<sub>2</sub>O<sub>3</sub>/MoS<sub>2</sub> sensor has a low LOD of 1 ppm with high response, as well as a short response/recovery time of 6 s/5 s, which is shorter than those of α-Fe<sub>2</sub>O<sub>3</sub> or MoS<sub>2</sub> devices. The enhancement performance of the α-Fe<sub>2</sub>O<sub>3</sub>/MoS<sub>2</sub> was attributed to the increased active sites for gas molecule





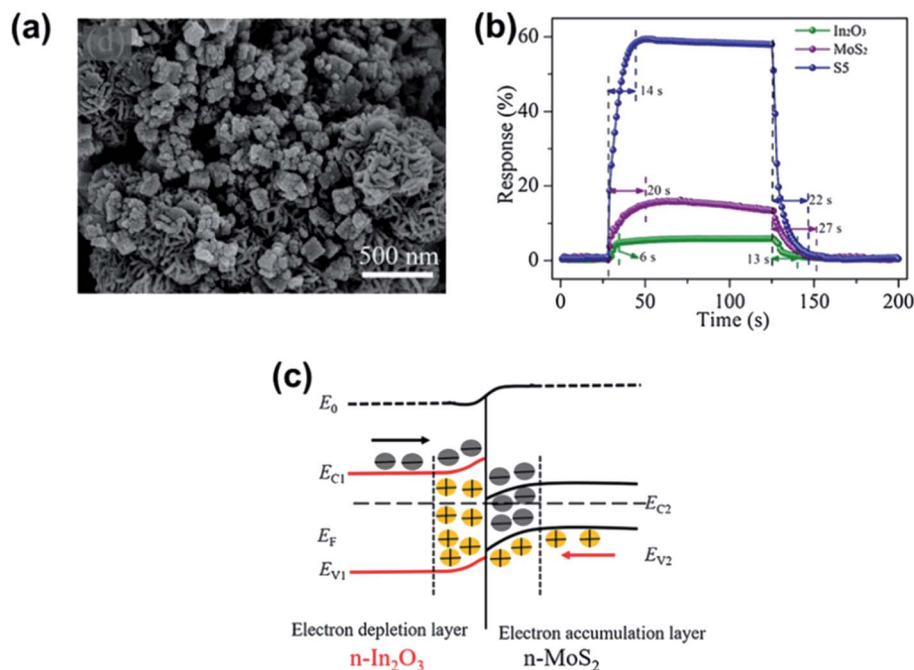


Fig. 21 (a) SEM images of  $\text{In}_2\text{O}_3$  nanocubes/flower-like  $\text{MoS}_2$  hybrids. (b) The response and recovery characteristics of  $\text{In}_2\text{O}_3$ ,  $\text{MoS}_2$  and  $\text{In}_2\text{O}_3/\text{MoS}_2$  (S5) film sensors exposed to 50 ppm HCHO gas. (c) The energy band diagram for the n-n junction of the  $\text{In}_2\text{O}_3/\text{MoS}_2$  film. Reprinted with permission from ref. 167. Copyright 2018, Elsevier.

adsorption, defects, or oxygen vacancies, when  $\alpha\text{-Fe}_2\text{O}_3$  into  $\text{MoS}_2$  nanosheets. Besides, Li *et al.*<sup>130</sup> modified CdS NWs with  $\text{CeO}_2$  NPs and found that the 5 wt%  $\text{CeO}_2/\text{CdS}$  n-n heterostructures exhibited a much higher response% toward 100 ppm ethanol (~5100%), which was 2.6 times larger than that of pure

CdS. The gas sensing properties of different metal sulfide-based ethanol sensors are listed in Table 5.

**4.1.6 Liquefied petroleum gas (LPG).** LPG is primarily composed of propane or butane and is widely used as fuels in vehicles, cooking, and heating appliances. LPG is potentially

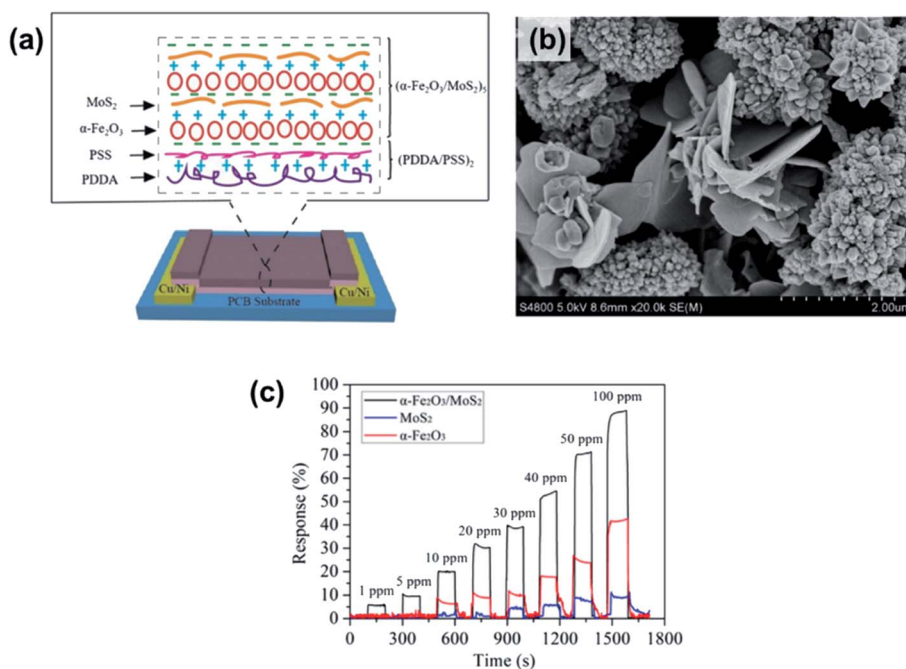


Fig. 22 (a) Schematic of an  $\alpha\text{-Fe}_2\text{O}_3/\text{MoS}_2$  gas sensor. (b) SEM image of the  $\alpha\text{-Fe}_2\text{O}_3/\text{MoS}_2$  nanocomposite. (c) Time-dependent response of the  $\alpha\text{-Fe}_2\text{O}_3/\text{MoS}_2$ ,  $\alpha\text{-Fe}_2\text{O}_3$ , and  $\text{MoS}_2$  film sensors towards various ethanol gas concentrations. Reprinted with permission from ref. 170. Copyright 2018, Elsevier.

Table 5 Gas sensing properties of metal sulfide-based sensors for ethanol

| Material                                                   | Structure          | Synthesis method                              | Concentration | Response (%) | LOD (ppm) | $\tau_s/\tau_r$ | OT (°C) | Ref. |
|------------------------------------------------------------|--------------------|-----------------------------------------------|---------------|--------------|-----------|-----------------|---------|------|
| SnS                                                        | NFKs               | Solid state reaction                          | 10 ppm        | 130          | —         | 2 s/9 s         | 200     | 34   |
| CdS                                                        | Thin film          | Screen printing                               | 5 ppm         | 6300         | —         | ~400 s/~400 s   | 300     | 171  |
| CuS                                                        | Hollow spheres     | Surfactant micelle-template inducing reaction | 800 ppm       | 1300*        | —         | 15 s/15 s       | 210     | 172  |
| $\beta$ -In <sub>2</sub> S <sub>3</sub>                    | Thin film          | Spray pyrolysis                               | 500 ppm       | 70*          | —         | 150 s/155 s     | 350     | 173  |
| MoS <sub>2</sub> /SnO <sub>2</sub>                         | Nanocomposites     | Hydrothermal method                           | 200 ppm       | 11 900*      | —         | ~20 s/~20 s     | 280     | 119  |
| MoS <sub>2</sub> /ZnO                                      | Nanocomposites     | Hydrothermal method                           | 50 ppm        | 4180*        | —         | ~20 s/~20 s     | 260     | 174  |
| 0D-MoS <sub>2</sub> /TiO <sub>2</sub>                      | p-n heterojunction | Hydrothermal method                           | 100 ppm       | 1320*        | —         | ~20 s/~15 s     | 150     | 175  |
| $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> /MoS <sub>2</sub> | Nanocomposite      | LBL self-assembly                             | 100 ppm       | 88.9         | 1         | 6 s/5 s         | RT      | 170  |
| CdS/CeO <sub>2</sub>                                       | NWs                | Solvothermal method                           | 100 ppm       | 5100*        | —         | 12 s/3 s        | 161     | 130  |

dangerous because it may cause suffocation or even an explosion when it leaks accidentally. Various types of heterojunctions were found to achieve a high gas response due to their nm-level crystalline size and the specific surface area. Patil *et al.*<sup>176</sup> reported an LPG sensor based on *p*-polyaniline/n-PbS heterojunctions, which showed a maximum response up to 70% at 0.06 vol% LPG at room temperature. As shown in Fig. 23, Ladhe *et al.* successfully proposed an n-Bi<sub>2</sub>S<sub>3</sub>/p-PbS<sup>177</sup> heterojunction for room temperature LPG sensors, which showed ~70% response towards 1000 ppm LPG with fast response and recovery time. Moreover, n-Bi<sub>2</sub>S<sub>3</sub>/p-CuSCN,<sup>178</sup> n-CdO/p-PbS,<sup>179</sup> n-CdS/p-PbS,<sup>180</sup> CdS/SnO<sub>2</sub>,<sup>181</sup> n-CdS/*p*-polyaniline,<sup>182</sup> and ZnS/polyacrylamide<sup>183</sup> demonstrated potential application in LPG detection. It is found that the alignment of energy bands at the interface of these heterojunctions shows the importance of gas sensing owing to the changes in barrier height of junction after exposure to the LPG gas environment.

## 4.2 Inorganic gases

Inorganic gases are essential for environment detection and as biomarkers in medical monitoring. The primary gases of interest are NH<sub>3</sub>, NO, NO<sub>2</sub>, CO<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>S, SO<sub>2</sub>, H<sub>2</sub>, and humidity. This section will discuss metal sulfide-based devices for the detection of various inorganic gases.

**4.2.1 NH<sub>3</sub>.** High concentrations of NH<sub>3</sub> could severely irritate the nose and throat of human beings and 1000 ppm vapours can cause pulmonary edema. Low concentrations of

NH<sub>3</sub> also could hurt the skin, eyes, and respiratory system after prolonged exposure.<sup>184</sup> Thus, the maximum permissible limit of NH<sub>3</sub> is 20 ppm for 8 hours.<sup>7</sup> Besides, NH<sub>3</sub> is present in the breath samples of healthy people and patients with renal disease. According to reports, the exhaled NH<sub>3</sub> concentration for healthy people ranges from 0.43 to 1.80 ppm, while that for end-stage renal disease patients ranges from 0.82 to 14.70 ppm.<sup>185</sup> Liu *et al.*<sup>186</sup> first presented high-performance room temperature chemical sensors based on Schottky-contact CVD MoS<sub>2</sub>. The devices showed a response% of 20% toward 20 ppb of NO<sub>2</sub> and 40% toward 1 ppm of NH<sub>3</sub>. The WS<sub>2</sub> NFK-based gas sensor showed *p*-type sensing behaviour and excellent response% of ~1500% towards 5 ppm NH<sub>3</sub> at room temperature.<sup>187</sup> Xiong *et al.*<sup>188</sup> fabricated an NH<sub>3</sub> sensor based on SnS<sub>2</sub> NFWS *via* a solvothermal process. The sensors exhibited a high response% of 640%, short response/recovery time of 40.6 s/624 s and a low LOD of 0.5 ppm NH<sub>3</sub>. Late *et al.*<sup>83</sup> compared and analyzed the gas sensing behaviours of single-layer (SL) and multilayer (ML) MoS<sub>2</sub> transistor-based sensors towards NO<sub>2</sub>, NH<sub>3</sub>, and humidity, see Fig. 17. They found that the SL-MoS<sub>2</sub> sensor was unstable; the 5L-MoS<sub>2</sub> sensor showed a stronger response to a bias voltage, and the gas sensing response was enhanced after applying gate voltage. Moreover, phototransistor gas sensors of WS<sub>2</sub> (ref. 189) and ReS<sub>2</sub> (ref. 190) were employed for NH<sub>3</sub> gas detection, whose response and recovery times were fast.

Table 6 Gas sensing properties of metal sulfide-based sensors for LPG gases

| Material                                  | Synthesis method                                       | Concentration (ppm) | Response (%) | LOD (ppm) | $\tau_s/\tau_r$ | OT (°C) | Ref. |
|-------------------------------------------|--------------------------------------------------------|---------------------|--------------|-----------|-----------------|---------|------|
| <i>p</i> -Polyaniline/n-PbS               | Chemical bath deposition and electrodeposition         | 780                 | 70           | —         | 125 s/200 s     | RT      | 176  |
| n-Bi <sub>2</sub> S <sub>3</sub> /p-CuSCN | Chemical deposition                                    | 1370                | 70           | —         | 180 s/142 s     | RT      | 178  |
| n-Bi <sub>2</sub> S <sub>3</sub> /p-PbS   | Successive ionic layer adsorption and reaction (SILAR) | 1000                | 72           | —         | 300 s/170 s     | RT      | 177  |
| n-CdO/p-PbS                               | SILAR                                                  | 1176                | 51.1         | —         | 150 s/134 s     | RT      | 179  |
| n-CdS/p-PbS                               | SILAR                                                  | 1200                | 60           | —         | 120 s/105 s     | RT      | 180  |
| CdS/SnO <sub>2</sub>                      | Screen printing                                        | 5000                | 7000         | —         | 40 s/110 s      | 200     | 181  |
| n-CdS/ <i>p</i> -polyaniline              | Electrodeposition                                      | 1040                | 80           | —         | 105 s/165 s     | RT      | 182  |
| ZnS/polyacrylamide                        | Thermal frontal polymerization                         | 5 vol%              | 62           | —         | 180 s/480 s     | RT      | 183  |
| PbS/polyacrylamide                        |                                                        |                     | 285          | —         | 120 s/300 s     |         |      |



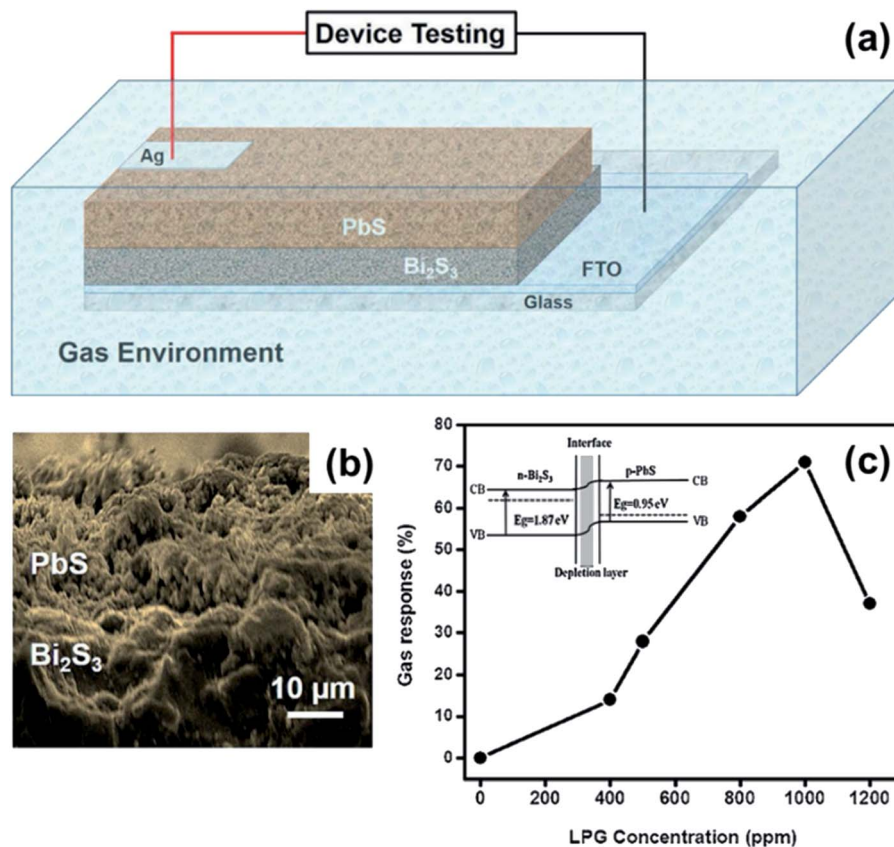


Fig. 23 (a) Schematic representation of the  $\text{n-Bi}_2\text{S}_3/\text{p-PbS}$  heterojunction device. (b) SEM image of the  $\text{n-Bi}_2\text{S}_3/\text{p-PbS}$  heterojunction. (c) The plot of variation in gas response (%) vs. LPG concentration (ppm) of the  $\text{n-Bi}_2\text{S}_3/\text{p-PbS}$  heterojunction. The inset shows the band diagram of the  $\text{n-Bi}_2\text{S}_3/\text{p-PbS}$  heterojunction. Reprinted with permission from ref. 177. Copyright 2017, Elsevier.

Benefitting from the interfacial Coulomb scattering and strong charge transfer, heterojunction-based devices have been used as  $\text{NH}_3$  gas sensors. Zhang *et al.*<sup>191</sup> prepared  $\text{MoS}_2/\text{ZnO}$  nanocomposites comprising ZnO NRs and  $\text{MoS}_2$  NSs, which could detect down to 12 ppb  $\text{NH}_3$ . Response/recovery times of 10 s/11 s were observed towards 50 ppm  $\text{NH}_3$  at room temperature. The first  $\text{MoS}_2/\text{Co}_3\text{O}_4$  nanocomposite  $\text{NH}_3$  sensor was

demonstrated by Sun *et al.*, which showed a high response of 10.3% towards 100 ppb  $\text{NH}_3$  with a response and recovery time of 98 s/100 s at room temperature, see Fig. 24a.<sup>192</sup> Moreover, an ultrahigh performance  $\text{NH}_3$  sensor based on a nanoporous  $\text{MoS}_2/\text{VS}_2$  heteroarchitecture was successfully fabricated. As shown in Fig. 24b, the gas-sensing performance investigated using a quartz crystal microbalance (QCM) reveals that  $\text{MoS}_2/$

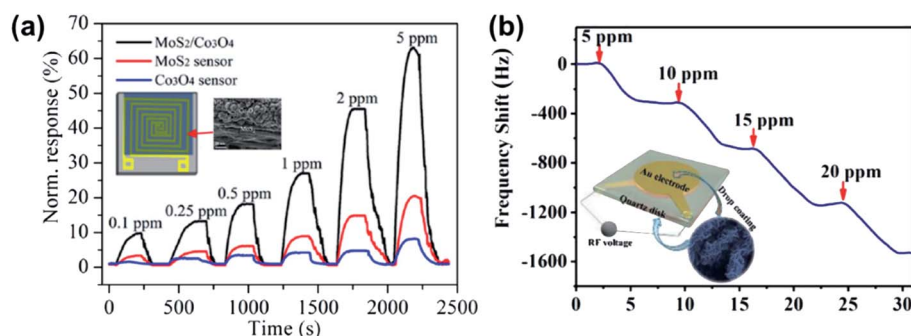


Fig. 24 (a) Normalized response of the  $\text{MoS}_2/\text{Co}_3\text{O}_4$ ,  $\text{MoS}_2$ , and  $\text{Co}_3\text{O}_4$  film sensors toward various  $\text{NH}_3$  concentrations (inset: the schematic of the  $\text{MoS}_2/\text{Co}_3\text{O}_4$  gas sensor and SEM image of  $\text{MoS}_2/\text{Co}_3\text{O}_4$ ). Reprinted with permission from ref. 192. Copyright 2017, ACS Publishing. (b) The mass-normalized time-dependent frequency shifts of  $\text{NH}_3$  adsorption on the  $\text{MoS}_2/\text{VS}_2$  heterostructure at  $40\ ^\circ\text{C}$  (inset: illustration of the QCM experimental sensor prepared via drop-coating of the  $\text{MoS}_2/\text{VS}_2$  heterostructure onto the Au electrode). Reprinted with permission from ref. 193. Copyright 2019, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

VS<sub>2</sub> exhibits a high adsorption uptake of  $\Delta f = 344.5$  Hz toward 5 ppm NH<sub>3</sub>, which is much better than that of previously reported QCM NH<sub>3</sub> sensors.<sup>193</sup> Other p–n heterojunction gas sensors, for instance, 2D WS<sub>2</sub> NSs decorated with TiO<sub>2</sub> QDs, were proved to have a high response to NH<sub>3</sub> gas at room temperature.<sup>194</sup> Xu *et al.*<sup>117</sup> and Leonardi *et al.*<sup>195</sup> synthesized SnO<sub>2</sub>–SnS<sub>2</sub> p–n heterojunctions by the oxidation of SnS<sub>2</sub> at high annealing temperature. The devices exhibited fast response time (11 s) at room temperature, much faster than that of other NH<sub>3</sub> sensors. For other heterojunction gas sensors, Pr–SnS<sub>2</sub>/ZnS,<sup>129</sup> PbS/TiO<sub>2</sub>,<sup>196</sup> and PbS/NaS<sub>2</sub> (ref. 197) were proposed as sensing materials for NH<sub>3</sub> detection. Pr–SnS<sub>2</sub>/ZnS showed a high response% of 1303% and fast response/recovery time of 6 s/13 s towards 50 ppm NH<sub>3</sub> at an OT of 160 °C, and PbS/NaS<sub>2</sub> had a high response% of 30 000% when exposed to 8.08% NH<sub>3</sub> at room temperature. The gas-sensing performances of various metal sulfide-based NH<sub>3</sub> gas sensors are listed in Table 7. It was found that the sensor based on metal oxide/metal sulfide heterojunctions exhibits higher response% and lower LOD.

**4.2.2 NO<sub>2</sub> and NO.** NO<sub>2</sub> is one of the most abundant air pollutants and is primarily emitted by fossil fuel burning, road traffic, indoor combustion,<sup>201</sup> and biomass burning.<sup>202</sup> It induces acid rain and photochemical smog. High concentrations of NO<sub>2</sub> can irritate the human respiratory system. Long exposures to low NO<sub>2</sub> concentrations also cause the development of asthma and respiratory symptoms. NO in exhaled breath is associated with inflammation of the air path, such as asthma and bronchiectasis. It is a typical biomarker for chronic obstructive pulmonary disease and nasal polyposis.<sup>203</sup> The

recommended concentration of NO for healthy people is below 25 ppb; when it is higher than 50 ppb, it is perhaps a sign of airway inflammation.<sup>204</sup> Notably, NO is easily oxidized to NO<sub>2</sub>, indicating that it is challenging to detect NO directly using semiconductor gas sensors. Sometimes, the concentration of NO is usually reflected indirectly by detecting NO<sub>2</sub>. Li *et al.*<sup>82</sup> proposed a MoS<sub>2</sub> FET NO sensor and compared and analyzed the sensors with monolayer, bilayer, trilayer, and quadrilayer MoS<sub>2</sub>. The response of the monolayer sensor is rapid and dramatic but unstable. In contrast, the multilayer sensors are stable and show sensitive responses down to a LOD of 0.8 ppm NO. TaS<sub>2</sub> NSs exfoliated by electrochemical lithium intercalation have been employed for the detection of NO and showed a high response% of 6000% towards 500 ppm NO and exhibited a sub-ppm LOD.<sup>60</sup> A TaS<sub>3</sub> nanofibre NO gas sensor exhibited a high sensitivity of 4.48° μM<sup>−1</sup> and a low LOD of 0.48 ppb, well under the allowed value set by the WHO, see Fig. 25.<sup>65</sup> The different types of NO and NO<sub>2</sub> gas sensors based on metal sulfides are summarised in Table 8.

Wang *et al.*<sup>33</sup> proposed a NO<sub>2</sub> gas sensor using large-sized SnS thin crystals, which present a high response% of 20% towards NO<sub>2</sub> at a 100 ppb concentration, as well as superior selectivity, low LOD (<100 ppb), and reversibility at room temperature. Benefitting from a large excitation Bohr radius (18 nm), PbS thin films were synthesized and applied in NO<sub>2</sub> detection, and they exhibited a response% of 35% for 50 ppm NO<sub>2</sub> at 150 °C with a rapid response time of 6 s.<sup>207</sup> Recently, Sonker *et al.*<sup>205</sup> used a sol–gel method for fabricating CdS NPs, which can detect 20 ppm NO<sub>2</sub> gas with a response% of 17 300%

Table 7 Literature study on the gas-sensing performance of metal sulfide-based NH<sub>3</sub> gas sensors

| Material                                         | Structure                                 | Synthesis method                 | Concentration | Response (%)          | LOD (ppm) | $\tau_s/\tau_r$        | OT (°C) | Ref. |
|--------------------------------------------------|-------------------------------------------|----------------------------------|---------------|-----------------------|-----------|------------------------|---------|------|
| MoS <sub>2</sub> (green illumination)            | Transistor                                | ME                               | 1000 ppm      | 86                    | —         | ~800 s/1500 s          | RT      | 83   |
| WS <sub>2</sub>                                  | NFKs                                      | Ball milling                     | 5 ppm         | ~1400*                | —         | ~120 s/~150 s          | RT      | 187  |
|                                                  | Phototransistor                           | ME                               | —             | —                     | —         | 2.6 s/56 s             | RT      | 189  |
| ReS <sub>2</sub>                                 | Phototransistor                           | ME                               | —             | —                     | —         | ~70 ms/~70 ms          | RT      | 190  |
| SnS <sub>2</sub>                                 | 2D SnS <sub>2</sub> with sulfur vacancies | Chemical exfoliation             | 500 ppm       | 420                   | —         | 16 s/450 s             | RT      | 109  |
|                                                  | NFWs                                      | Solvothermal method              | 100 ppm       | 640*                  | 0.5       | 40.6 s/624 s           | 200     | 188  |
|                                                  | NFWs                                      | Hydrothermal method              | 5 ppm         | 21.6                  | —         | 40–50 s/100–120 s      | RT      | 198  |
| Graphene/MoS <sub>2</sub>                        | Heterostructure                           | ME–MoS <sub>2</sub> CVD-graphene | 100 ppm       | 6                     | —         | NA/30 min              | 150     | 199  |
| MoS <sub>2</sub> /ZnO                            | Nanocomposites                            | LBL self-assembly                | 50 ppm        | 46.2                  | 0.012     | 10 s/11 s              | RT      | 191  |
| MoS <sub>2</sub> /CuO                            | Nanoworms                                 | Sputtering                       | 100 ppm       | 47                    | 5         | 17 s/26 s              | RT      | 200  |
| MoS <sub>2</sub> /Co <sub>3</sub> O <sub>4</sub> | Nanocomposites                            | LBL self-assembly                | 0.1 ppm       | 10.3                  | 0.1       | 98 s/100 s             | RT      | 192  |
| MoS <sub>2</sub> /VS <sub>2</sub>                | Heterostructure, QCM                      | Hydrothermal method              | 5 ppm         | $\Delta f = 344.5$ Hz | —         | —                      | 40      | 193  |
| WS <sub>2</sub> /TiO <sub>2</sub>                | Nanocomposites                            | Mixture solution                 | 500 ppm       | 56.69                 | 20        | 200 s/174.43 ± 13.75 s | RT      | 194  |
| SnS <sub>2</sub> /SnO <sub>2</sub>               | NFKs                                      | Annealing                        | 50 ppm        | 40*                   | —         | ~60 s/~300 s           | 130     | 195  |
|                                                  | Hybrids                                   | Oxidation                        | 10 ppm        | 16*                   | —         | 11 s/NA                | RT      | 117  |
| Pr–SnS <sub>2</sub> /ZnS                         | NFWs                                      | Hydrothermal method              | 50 ppm        | 1303*                 | —         | 6 s/13 s               | 160     | 129  |
| PbS QDs/TiO <sub>2</sub>                         | NTs                                       | SILAR                            | 100 ppm       | 1649*                 | 2         | ~10 s/~10 s            | RT      | 196  |
| PbS/NaS <sub>2</sub>                             | NPs                                       | —                                | 8.08%         | 30 000*               | —         | 46 s/67 s              | RT      | 197  |





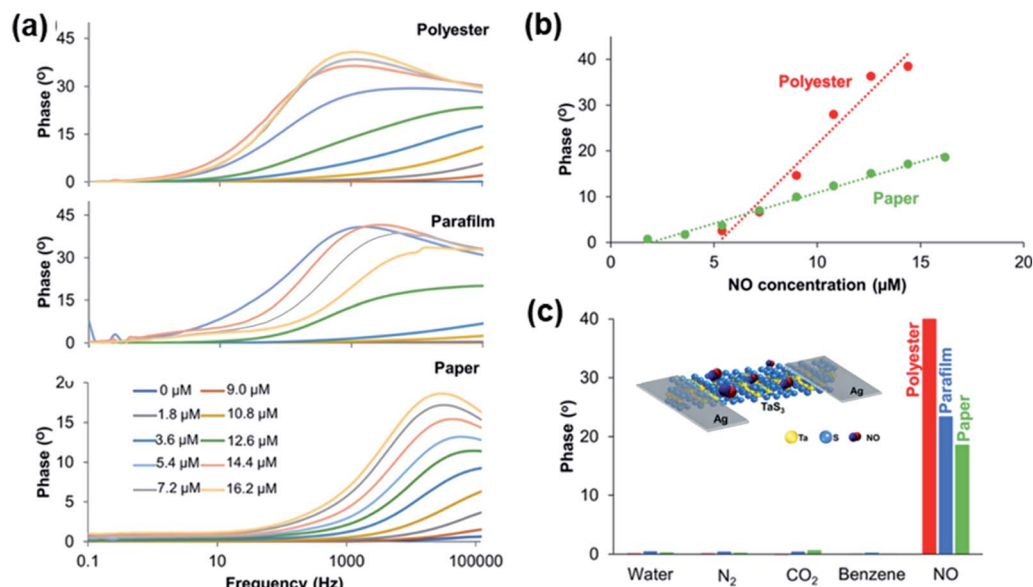


Fig. 25 (a) Impedance responses of the TaS<sub>3</sub> sensor fabricated in polyester, parafilm, and paper under different NO concentrations from 0 to 16.2 μM. (b) Calibration curves of the TaS<sub>3</sub> gas sensor fabricated in polyester and paper at different NO concentrations. (c) Selectivity study comparison of the TaS<sub>3</sub> gas sensor fabricated in all configurations (paper, parafilm, and polyester). The inset image shows the schematic representation of various TaS<sub>3</sub> nanofiber-based devices. Reprinted with permission from ref. 65. Copyright 2018, ACS Publishing.

at 70 °C. Donarelli *et al.*<sup>29</sup> found that LPE-MoS<sub>2</sub> NFKs after annealing in air at 150 °C and 250 °C can show a p-type and n-type conductivity, respectively. The p-type MoS<sub>2</sub> showed 15% response towards 1 ppm with fast response/recovery time (11 s/22 s), while the n-type MoS<sub>2</sub> exhibited a higher response% of 480% and a lower LOD of 20 ppb. Xu *et al.*<sup>208</sup> synthesized ultra-thin WS<sub>2</sub> NSs through a hydrothermal and calcination process, which showed a high response of 9.3% after exposure to 0.1 ppm NO<sub>2</sub> gas at room temperature. Ko *et al.*<sup>211</sup> proved that the WS<sub>2</sub> gas sensor showed dramatically improved response (667%) and recovery upon NO<sub>2</sub> exposure after functionalization with AgNWs. Another WS<sub>2</sub>/WO<sub>3</sub>-based gas sensor showed an excellent LOD of 40 ppb in dry air for NO<sub>2</sub> at an OT of 150 °C.<sup>215</sup> 2D SnS<sub>2</sub>-based gas sensors presented a high response% of 3533% toward 10 ppm NO<sub>2</sub> and showed highly selective and reversible NO<sub>2</sub> sensing.<sup>210</sup> Kim *et al.*<sup>59</sup> fabricated a room temperature NO<sub>2</sub> sensor using 2D NbS<sub>2</sub>, which showed a response% of 2832% toward 10 ppm NO<sub>2</sub> and a low LOD of 241.02 ppb.

For metal-metal sulfide Schottky junctions, Liu *et al.*<sup>186</sup> observed a considerable SB in the Ti/Au electrodes and at the CVD-MoS<sub>2</sub> contact interface, which showed a conductance change of 2–3 orders of magnitude upon exposure to sub-ppb level concentrations of NO<sub>2</sub> and NH<sub>3</sub>. Besides, vdW vertical Schottky junctions of graphene and semiconductors have attracted considerable attention as emerging transducers for gas sensors. Tabata *et al.*<sup>212</sup> deeply analyzed the NO<sub>2</sub> gas-sensing performance of a graphene/MoS<sub>2</sub>-based gas sensor, where the SBH was modulated by bias- and gate-voltage. The device exhibited an ultra-high response% of 160 000% after 10 min exposure to NO<sub>2</sub>. To know the difference between the Schottky junction of metal-metal sulfides and graphene-metal sulfides,

Pham *et al.*<sup>114</sup> compared and analyzed the gas-sensing performances of CVD MoS<sub>2</sub> with Au metal electrodes (Au-MoS<sub>2</sub>-Au), graphene electrodes (Gr-MoS<sub>2</sub>-Gr), and graphene/Au electrodes (Au/Gr-MoS<sub>2</sub>-Gr/Au). The resulting Au/Gr-MoS<sub>2</sub>-Gr/Au gas sensor under red light illumination showed a significant enhancement of the device response% toward 150 ppb of NO<sub>2</sub> gas reaching 500% (see Fig. 26). The excellent performance could be attributed to the encapsulation of graphene electrodes with the Au layer affecting the work function of graphene, resulting in an increasing SBH. Furthermore, Au/Gr electrodes could hinder the negative effects of the modulation of the work function induced by the doped graphene with NO<sub>2</sub> molecules.

For heterojunction-based devices, MoS<sub>2</sub>/SnO<sub>2</sub> p-n heterojunctions were constructed and used for ethanol, TMA, and NO<sub>2</sub> gas sensing.<sup>119–121</sup> They exhibited high sensitivity, lower OT, excellent sensing selectivity, and outstanding long-term stability. Shao *et al.*<sup>114</sup> fabricated rGO-MoS<sub>2</sub>-CdS nanocomposite films *via* solvothermal treatment and analyzed the sensing performance. The results showed a largely enhanced sensor response of 27.4% toward 0.2 ppm NO<sub>2</sub>, approximately 7 times higher than the value for the rGO-MoS<sub>2</sub> based gas sensor. Moreover, a SnO<sub>2</sub>-SnS<sub>2</sub> p-n heterojunction was employed in the NO<sub>2</sub> gas sensor.<sup>117,148</sup>

A FET gas sensor was used for NO<sub>2</sub> gas sensing because the conductance of the channel can be modulated by applying different bias voltages on the gate electrode. Late *et al.*<sup>83</sup> analyzed the NO<sub>2</sub> sensing behaviours of the MoS<sub>2</sub> transistor, Fig. 17. The response was enhanced after applying gate bias. Similarly, WS<sub>2</sub> (ref. 189) and ReS<sub>2</sub> (ref. 190) FETs were employed to detect different gases, such as O<sub>2</sub>, NH<sub>3</sub>, and NO<sub>2</sub>. As mentioned in Section 3.5, the strong electron transfer between the FET channel materials and the gas molecule could alter the

carrier concentration of the channel, modulate the mobility, further affect semiconductor work function, and finally change the current of the FET.<sup>221,222</sup> Based on this mechanism, our group analyzed a WS<sub>2</sub>/IGZO p–n junction-based gas sensor in chemiresistor and transistor mode, respectively.<sup>217</sup> It was found that the transistor shows an ultra-high response after exposure to NO<sub>2</sub>, with a response% of 499 400% for 300 ppm, which is ~27 times higher than that in chemiresistor mode (see Fig. 27a–c). One special case reported by Tabata *et al.*<sup>212</sup> is the graphene/MoS<sub>2</sub> heterojunction (GMH) sensor. As shown in Fig. 27d–f, the device had a high response% to NO<sub>2</sub> of 160 000% at a 0 V back-gate voltage ( $V_{BG}$ ); however, when  $V_{BG}$  = 40 V, the response% decreased to 600%. They found that the drain current was

primarily determined by the SBH at the counter Schottky diode of the MoS<sub>2</sub>/Ti contact, and the NO<sub>2</sub>-induced modulation in the SBH at the GMH was not reflected in the sensor response. Last but not least, the SAW NO<sub>2</sub> sensor uses SnS CQDs as the sensing layer and is fabricated on a quartz substrate.<sup>140</sup> The sensor could detect a low concentration of NO<sub>2</sub> gas at room temperature with a good efficiency and selectivity (see Fig. 19).

**4.2.3 CO<sub>2</sub> and O<sub>2</sub>.** CO<sub>2</sub> is the fourth most abundant component of dry air. Tests have shown that 5% CO<sub>2</sub> is not harmful to humans if sufficient oxygen is present, but once the O<sub>2</sub> concentration is less than 17%, even 4% CO<sub>2</sub> can cause severe poisoning. Considering that the ambient concentration of CO<sub>2</sub> is approximately 0.03%, the required LOD for CO<sub>2</sub>

Table 8 Literature study on the NO<sub>x</sub> sensing performance of metal sulfide-based devices

| Material                           | Structure        | Synthesis method                             | Analyte         | Concentration (ppm) | Response (%)                         | LOD        | $\tau_s/\tau_r$        | OT (°C)          | Ref. |
|------------------------------------|------------------|----------------------------------------------|-----------------|---------------------|--------------------------------------|------------|------------------------|------------------|------|
| SnS                                | Thin crystal     | Solvothermal method                          | NO <sub>2</sub> | 0.1                 | 20                                   | —          | NA/5 s                 | RT               | 33   |
| CdS                                | Thin film        | Chemical route                               | NO <sub>2</sub> | 20                  | 17 300                               | —          | 331 s/207 s            | 70               | 205  |
|                                    | Thin film        | Chemical bath deposition                     | NO <sub>2</sub> | 200                 | 61                                   | —          | 50 s/NA                | RT               | 206  |
| PbS                                | Thin film        | Chemical bath deposition                     | NO <sub>2</sub> | 100                 | 74                                   | —          | 20 s/36 s              | 38               | 100  |
|                                    | Thin film        | SILAR                                        | NO <sub>2</sub> | 50                  | 35                                   | —          | 6 s/97 s               | 150              | 207  |
| TaS <sub>2</sub>                   | NSs              | Electrochemical lithium-intercalation        | NO              | 5                   | 60                                   | —          | —                      | RT               | 60   |
| TaS <sub>3</sub>                   | Nanofibres       | Vapour-phase growth                          | NO              | —                   | Sensitivity 4.48° $\mu\text{M}^{-1}$ | 0.48 ppb   | —                      | RT               | 65   |
| MoS <sub>2</sub>                   | Transistor       | ME                                           | NO              | 2                   | 80                                   | 0.8 ppm    | —                      | RT               | 82   |
|                                    | Transistor       | ME                                           | NO <sub>2</sub> | 1000                | 1372                                 | —          | ~800 s/1500 s          | RT (green light) | 83   |
|                                    | NFKs             | LPE                                          | NO <sub>2</sub> | 1                   | 15 (p-type)<br>480 (n-type)          | 20 ppb     | 11 s/22 s<br>41 s/39 s | 200              | 29   |
| WS <sub>2</sub>                    | NSs              | Hydrothermal method & calcination            | NO <sub>2</sub> | 0.1                 | 9.3                                  | 100 ppb    | 5 min/25 min           | RT               | 208  |
| SnS <sub>2</sub>                   | 2D               | Ball milling                                 | NO <sub>2</sub> | 10                  | 2000                                 | —          | 6/40 s                 | 250              | 209  |
|                                    | 2D flakes        | Solvothermal method                          | NO <sub>2</sub> | 10                  | 3533*                                | —          | ~170 s/~140 s          | 120              | 210  |
| NbS <sub>2</sub>                   | NSs              | CVD                                          | NO <sub>2</sub> | 10                  | 2832                                 | 241.02 ppb | 3000 s/9000 s          | RT               | 59   |
| Ag NWs–WS <sub>2</sub>             | NSs              | ALD                                          | NO <sub>2</sub> | 500                 | 667                                  | —          | 5 min/10 min           | RT               | 211  |
| Al/MoS <sub>2</sub>                | Schottky contact | CVD                                          | NO <sub>2</sub> | 10                  | 60                                   | —          | ~5 min/~20 min         | RT               | 111  |
| Au/Gr–MoS <sub>2</sub> –Gr/Au      | Schottky contact | CVD                                          | NO <sub>2</sub> | 0.15                | 500*                                 | 0.1 ppb    | ~1000 s/~700 s         | RT (red light)   | 114  |
| Gr–MoS <sub>2</sub>                | Schottky contact | ME                                           | NO <sub>2</sub> | 1                   | 160 000                              | —          | —                      | RT               | 212  |
| MoS <sub>2</sub> /SnO <sub>2</sub> | Heterostructures | Chemical methods                             | NO <sub>2</sub> | 5                   | 1770*                                | —          | 74 s/NA                | RT               | 121  |
| MoS <sub>2</sub> /ZnO              | NWs              | Hydrothermal method & CVD                    | NO <sub>2</sub> | 50                  | 31.2                                 | 0.2 ppm    | 60 min/65 min          | 200              | 213  |
| rGO–MoS <sub>2</sub> –CdS          | Nanocomposite    | Hydrothermal method                          | NO <sub>2</sub> | 0.2                 | 27.4                                 | —          | 25 s/34 s              | 75               | 214  |
| WS <sub>2</sub> /WO <sub>3</sub>   | Nanocomposites   | Oxidation                                    | NO <sub>2</sub> | 0.4                 | 100*                                 | 400 ppb    | —                      | 150              | 215  |
| WS <sub>2</sub> /ZnS               | Heterostructures | LPE–WS <sub>2</sub> , chemical method        | NO <sub>2</sub> | 5                   | 3150*                                | 10 ppb     | 4 s/~400 s             | RT               | 216  |
| WS <sub>2</sub> /IGZO              | Heterojunction   | CVD, sputtering                              | NO <sub>2</sub> | 5                   | 6820                                 | 26 ppb     | —                      | RT               | 217  |
|                                    |                  |                                              |                 | 300                 | 499 400                              |            |                        |                  |      |
| SnS <sub>2</sub> /SnO <sub>2</sub> | Nanocomposites   | Oxidation                                    | NO <sub>2</sub> | 8                   | 430*                                 | 1 ppm      | 159 s/297 s            | 80               | 148  |
| SnS <sub>2</sub> /SiO <sub>2</sub> | Nanograins       | CVD                                          | NO <sub>2</sub> | 10                  | 701                                  | 408.9 ppb  | 272.8 s/3800.4 s       | RT               | 218  |
| SnS <sub>2</sub> /rGO              | Heterojunction   | Hydrothermal method                          | NO <sub>2</sub> | 8                   | 49.8                                 | 8.7 ppb    | NA/76 s                | RT               | 219  |
| PbS QDs/MoS <sub>2</sub>           | Nanocomposites   | Hydrothermal method & chemical precipitation | NO <sub>2</sub> | 100                 | ~23                                  | —          | 30 s/235 s             | RT               | 220  |
| ZnS/CuO                            | NWs              | Thermal evaporation & solvothermal method    | NO <sub>2</sub> | 5                   | 955*                                 | —          | 45 s/170 s             | RT (UV light)    | 133  |



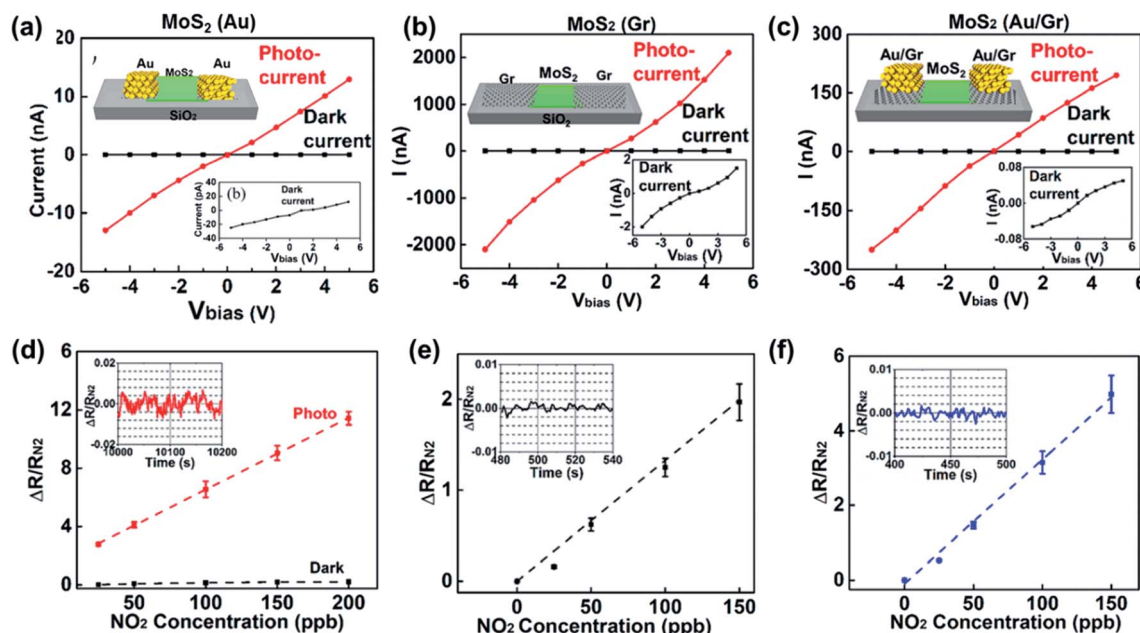


Fig. 26  $I$ - $V$  curves under red LED illumination (red line) and in the dark (black line) of (a) Au- $\text{MoS}_2$ -Au, (b) Gr- $\text{MoS}_2$ -Gr, and (c) Au/Gr- $\text{MoS}_2$ -Gr/Au devices. The insets show the corresponding schematics of the devices and expanded  $I$ - $V$  curves in the dark. (d-f) Dependence of the normalized amplitude of the resistance change of (d) Au- $\text{MoS}_2$ -Au, (e) Gr- $\text{MoS}_2$ -Gr, and (f) Au/Gr- $\text{MoS}_2$ -Gr/Au devices on the concentration of  $\text{NO}_2$  gas. The inset image shows a temporal trace of the experimentally recorded noise of  $\Delta R/R_0$ . All data were collected under a dc bias of 5 V. Reprinted with permission from ref. 114. Copyright 2019, ACS Publishing.

sensors could be at the ppm-level. Because  $\text{CO}_2$  is a kind of nonpolar gas owing to its linear and symmetrical structure, the adsorption energy between  $\text{CO}_2$  and the surface of metal sulfides is low. To this end, a new optical  $\text{CO}_2$  sensor based on the colorimetric change of the pH indicator  $\alpha$ -naphtholphthalein with the internal reference fluorescent CIS/ZnS QDs was developed.<sup>223,224</sup> The experimental result reveals that the new optical  $\text{CO}_2$  sensor has a response% of  $(I_{100} - I_0)/I_0 \times 100\% = 1240\%$ . Similarly, Chu *et al.*<sup>225</sup> developed a CdSe/ZnS QD based

optical fibre  $\text{CO}_2$  sensor, which showed a high response% of  $(R_0 - R)/R \times 100\% = 84\%$  and exhibited a uniquely linear response to  $\text{CO}_2$  concentrations in the range of 0–100%. The gas testing setup of the fibre-optic  $\text{CO}_2$  sensor is shown in Fig. 28, and this testing method can quantitatively measure the  $\text{CO}_2$  concentration; however, it cannot detect changes of the fluorescence spectra in real-time.

$\text{O}_2$  is a major component of air and greatly affects metal corrosion protection, fuel combustion, and food storage. It is

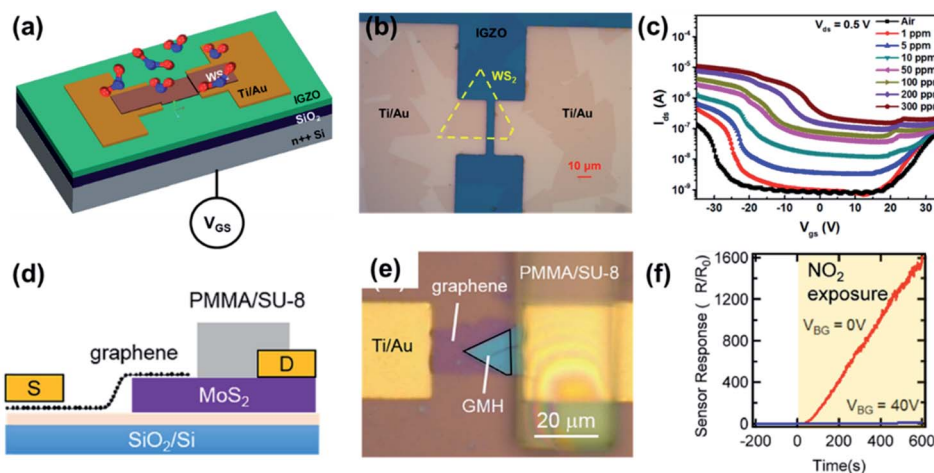


Fig. 27 (a) Schematic diagram and (b) optical image of the  $\text{WS}_2/\text{IGZO}$  transistor. (c) Transfer curves of the  $\text{WS}_2/\text{IGZO}$  transistor under different  $\text{NO}_2$  concentrations. Reprinted with permission from ref. 217. Copyright 2019, ACS Publishing. (d) Schematic diagram and (e) optical image of the graphene/ $\text{MoS}_2$  heterojunction (GMH) device with a gas barrier layer. (f) Time-dependent sensor responses of GMH under different gate voltages ( $V_{\text{BG}} = 0$  and  $40$  V). Reprinted with permission from ref. 212. Copyright 2019, ACS Publishing.

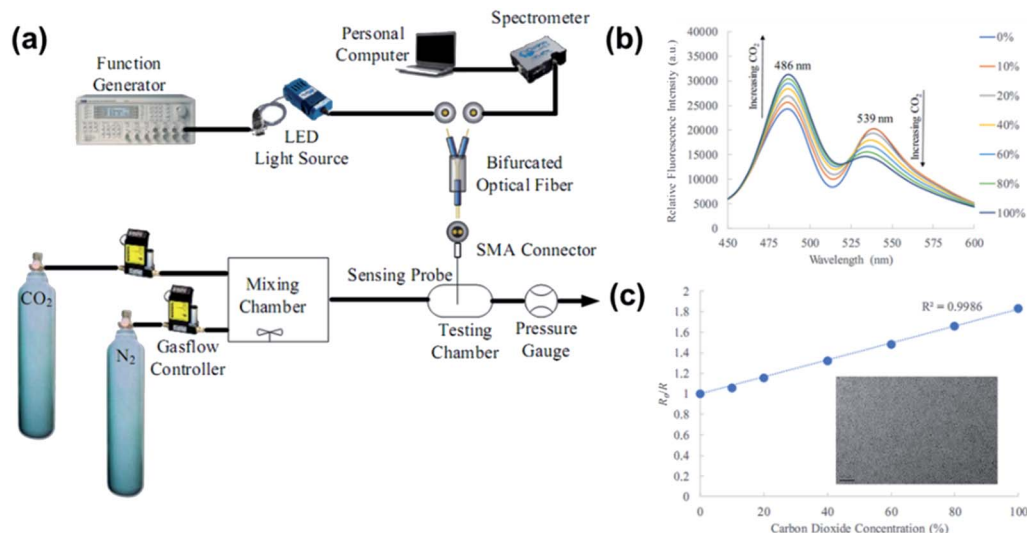


Fig. 28 (a) Experimental setup for the ratiometric optical fibre CO<sub>2</sub> sensing. (b) Fluorescence spectra of the ratiometric optical fibre sensor under different CO<sub>2</sub> concentrations. (c) Calibration curve of the ratiometric optical fibre CO<sub>2</sub> sensor at 0–100% concentration. Reprinted with permission from ref. 225. Copyright 2019, SPIE publishing.

essential to monitor the O<sub>2</sub> content in industrial production and medical care. Metal sulfide nanomaterials for O<sub>2</sub> sensing have not been extensively studied. Kim *et al.*<sup>226</sup> prepared MoS<sub>2</sub> NP-based gas sensors through LPE methods and investigated their O<sub>2</sub> sensing behaviour, which showed a high response% of 769% towards a 2% concentration of O<sub>2</sub> and a low LOD at the ppb level. Li *et al.*<sup>227</sup> proposed a 2D SnS<sub>2</sub>-based sensor, which provided high and reversible responses to O<sub>2</sub> pulses in the range of 0 to 20% volume in the dark at 150 °C. They applied UV irradiation for improving the O<sub>2</sub> sensing performance. Karami *et al.*<sup>228</sup> synthesized SnS–SnO<sub>2</sub> nanocomposites and used them as O<sub>2</sub> gas-sensing agents, which showed a high dynamic range, high sensitivity to O<sub>2</sub>, fast response time, and low memory effect without any interference from the other gases (OT = 128 °C).

**4.2.4 H<sub>2</sub>S and SO<sub>2</sub>.** Both H<sub>2</sub>S and SO<sub>2</sub> are hazardous gases and atmospheric pollutants. H<sub>2</sub>S smells like rotten eggs and irritates people's eyes, nose, and throat. Long-term exposure to H<sub>2</sub>S above 100 ppm can cause death. In the human body, H<sub>2</sub>S is

a kind of metabolic product that has an unpleasant odor and is associated with halitosis. SO<sub>2</sub> is highly corrosive and easily oxidized to create sulfuric acid in the air. These two gases pose significant threats to the environment and human health and require accurate measurement.

PbS CQDs have been used as H<sub>2</sub>S gas sensing materials, and they exhibit a response% of 421 700% towards 50 ppm H<sub>2</sub>S, which is considerably high, and a fast response/recovery time of 23 s/171 s.<sup>101</sup> Metal oxide/metal sulfide heterojunctions, such as ZnS/ZnO<sup>132</sup> and CuS/CuO,<sup>229</sup> have been employed for the detection of H<sub>2</sub>S gas, see Fig. 29. Souda and Shimizu<sup>106</sup> tested various metal monosulfide-based gas sensors (NiS, CdS, SnS, and PbS), which showed a high SO<sub>2</sub> response at 300–400 °C. The CdS-based sensor has the best sensing performance, whose response was almost linear with the logarithm of SO<sub>2</sub> concentration between 20 and 200 ppm. It has a 90% response% to 100 ppm SO<sub>2</sub> but the response time is as long as 2–4 min and it works at 400 °C. Zhang *et al.*<sup>90</sup> fabricated a room-temperature

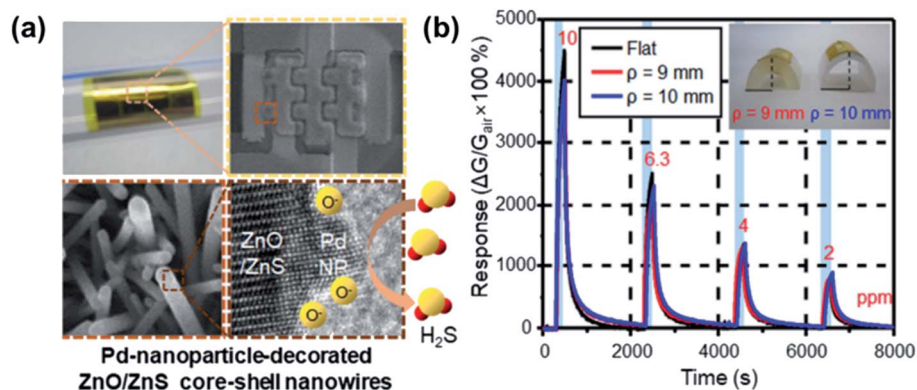


Fig. 29 (a) Photograph and SEM and TEM images of a ZnO/ZnS NW sensor on a flexible substrate and (b) the H<sub>2</sub>S gas sensing result. Reprinted with permission from ref. 132. Copyright 2019, ACS Publishing.



SO<sub>2</sub> sensor using metal-doped MoS<sub>2</sub> NFWs. The Ni-doped MoS<sub>2</sub> showed the best performance among different metal-doped MoS<sub>2</sub> (*i.e.*, Ni-, Fe-, Co-doped MoS<sub>2</sub>) compounds and showed a 7.4% response% toward 5 ppm SO<sub>2</sub> and a low LOD of 250 ppb. Table 9 summarises the gas sensing properties of metal sulfide-based sensors for CO<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>S, and SO<sub>2</sub>. It is clear that PbS is an ideal candidate for H<sub>2</sub>S gas detection, and there is room for functionalized MoS<sub>2</sub> for the detection of other types of gases (*i.e.*, SO<sub>2</sub> and O<sub>2</sub>).

**4.2.5 H<sub>2</sub>.** H<sub>2</sub> is a colorless, tasteless, odorless, and flammable gas. It is an excellent candidate carrier in the clean energy area, such as for automobile engines and fuel cells. Thus it requires high-performance H<sub>2</sub> sensors in mobile transportation as well as household environments. Hafeez *et al.*<sup>231</sup> compared and analyzed the H<sub>2</sub> gas-sensing performance of ZnS nanostructures with different morphologies (NWs, nanodots

(NDs), and nanoleaves (NLs)). They found that NWs have higher cohesive energy than others, which showed a response% of 800% towards 50 000 ppm H<sub>2</sub> gas at an OT of 230 °C. Sabah *et al.*<sup>104</sup> prepared a CuS thin film by spray pyrolysis deposition using deionized water and used it for the detection of H<sub>2</sub> gases. Linganisio *et al.*<sup>105</sup> synthesized NiS nanostructures and measured the H<sub>2</sub> gas sensitivity, which has 158% response to 100 ppm H<sub>2</sub> at 300 °C. Baek and Kim<sup>107</sup> fabricated an H<sub>2</sub> sensor with few-layered Pd-doped MoS<sub>2</sub>, which exhibited a 35.3% response% when exposed to a 1% H<sub>2</sub>-containing gas. In contrast, the pristine MoS<sub>2</sub> showed no reaction. Perrozzi *et al.*<sup>215</sup> demonstrated that the H<sub>2</sub> gas sensor based on WS<sub>2</sub>/WO<sub>3</sub> hierarchical heterostructures with surface oxygen and sulfur vacancies had a high response% of 430% towards 500 ppm H<sub>2</sub> and exhibited a low LOD of 1 ppm. The sensors showed no substantial humidity cross-sensitivity effects, indicating the

Table 9 Gas sensing properties of metal sulfide-based sensors for inorganic gases

| Material                  | Structure     | Synthesis method           | Analyte          | Concentration | Response (%) | LOD       | $\tau_s/\tau_r$ | OT (°C)  | Ref. |
|---------------------------|---------------|----------------------------|------------------|---------------|--------------|-----------|-----------------|----------|------|
| CIS/ZnS (optical)         | QDs           | Hydrothermal method        | CO <sub>2</sub>  | 100 vol%      | 1240*        | —         | —               | RT       | 223  |
|                           | QDs           | Hydrothermal method        |                  | 100 vol%      | 99.6         | —         | —               | RT       | 224  |
| CdSe/ZnS (optical)        | QDs           | Hydrothermal method        | CO <sub>2</sub>  | 100 vol%      | 84*          | —         | —               | RT       | 225  |
| MoS <sub>2</sub>          | NPs           | Chemical exfoliation       | O <sub>2</sub>   | 2 vol%        | 769*         | 49.96 ppb | —               | 300      | 226  |
| GaS                       | NSs           | ME                         | O <sub>2</sub>   | —             | —            | —         | —               | —        | 230  |
| SnS <sub>2</sub>          | 2D flakes     | Wet-chemical method        | O <sub>2</sub>   | 2 vol%        | 160*         | —         | 10 min/15 min   | 130 (UV) | 227  |
| SnS-SnO <sub>2</sub>      | Nanocomposite | Electrochemical deposition | O <sub>2</sub>   | 19 ppm        | 21 000       | 900 ppb   | 52 s/38 s       | 128      | 228  |
| PbS                       | QDs           | Deposition                 | H <sub>2</sub> S | 500 ppm       | 421 700*     | —         | 23 s/171 s      | 135      | 101  |
| CuS/CuO                   | Nanocomposite | Solvothermal method        | H <sub>2</sub> S | 1.88%         | 313 900      | —         | 75 s/67 s       | RT       | 229  |
| ZnS/ZnO                   | Nanocomposite | Hydrothermal method        | H <sub>2</sub> S | 10 ppm        | 4491         | —         | 99 s/88 s       | 95       | 132  |
| CdS                       | 2D flakes     | Wet-chemical method        | SO <sub>2</sub>  | 100 ppm       | —            | —         | 15 min/NA       | 400      | 106  |
| Ni-doped MoS <sub>2</sub> | NFWs          | Hydrothermal method        | SO <sub>2</sub>  | 5 ppm         | 7.4          | 250 ppb   | 51 s/73 s       | RT       | 90   |

Table 10 Gas sensing properties of metal sulfide-based sensors for H<sub>2</sub>

| Material                         | Structure      | Synthesis method    | Concentration | Response (%) | LOD (ppm) | $\tau_s/\tau_r$ | OT (°C) | Ref. |
|----------------------------------|----------------|---------------------|---------------|--------------|-----------|-----------------|---------|------|
| ZnS                              | Nanostructures | PVD                 | 50 000 ppm    | 800          | —         | —               | 230     | 231  |
| CuS                              | Film           | Spray pyrolysis     | 1000 ppm      | 9890         | —         | 16/34 s         | RT      | 104  |
| Au-coated NiS                    | Nanostructures | Hydrothermal method | 95%           | 58*          | —         | ~50 s/~100 s    | 300     | 105  |
| Pd-doped MoS <sub>2</sub>        | NSs            | Solution processing | 1%            | 35.3         | 50        | ~500 s/~1200 s  | RT      | 107  |
| WS <sub>2</sub> /WO <sub>3</sub> | Nanocomposites | Oxidation           | 500 ppm       | 430*         | 1         | —               | 150     | 215  |

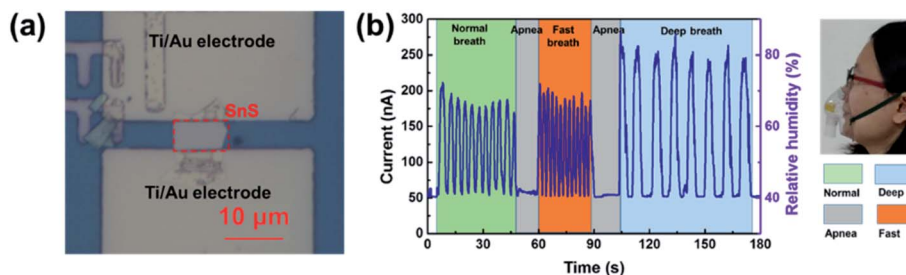


Fig. 30 (a) Optical image of a SnS nanoflake-based sensor. (b) Real-time respiration detection by using a SnS humidity sensor. Reprinted with permission from ref. 71. Copyright 2019, © IOP Publishing. All rights reserved.



**Table 11** The humidity sensing performances of fibre-optic sensing devices in the literature

| Device structure              | $\tau_s$ (s) | $\tau_r$ (s) | Dynamic range of response | Ref. |
|-------------------------------|--------------|--------------|---------------------------|------|
| MoS <sub>2</sub> -coated ESMF | 0.066        | 2.395        | 0.487 dB/(20–80% RH)      | 237  |
| MoS <sub>2</sub> -coated SPF  | 0.85         | 0.85         | 13.5 dB/(40–85% RH)       | 138  |
| WS <sub>2</sub> -coated SPF   | 1            | 4            | 9 dB/(37–90% RH)          | 236  |

great potential application in real-world H<sub>2</sub> detection. Various metal sulfide-based H<sub>2</sub> gas sensors are listed in Table 10.

**4.2.6 Humidity sensor.** Humidity sensors have been successfully used in various fields, such as environmental monitoring, industrial production, and the medical instrumentation field. Tang *et al.*<sup>71</sup> demonstrated that SnS NFKs could be used for real-time respiration detection due to their high response% of 2 491 000% and fast response/recovery time (6 s/4 s), suitable for health monitoring, see Fig. 30. Guo *et al.* fabricated transparent and flexible WS<sub>2</sub> based humidity sensors for electronic skin, with a wide relative humidity range (up to 90%) with fast response and recovery in a few seconds.<sup>232</sup> Feng *et al.*<sup>233</sup> fabricated a flexible touchless positioning interface based on a highly sensitive VS<sub>2</sub> NS humidity sensor. However, VS<sub>2</sub> ultra-thin NSs have poor stability. To improve the stability, Chen *et al.* proposed a MoS<sub>2</sub>/VS<sub>2</sub> (ref. 35) sensor; after 30 days its response% was maintained at around 579 750%, indicating that the nanocomposite sensor has good long-term stability. Chemiresistor sensors based on ReS<sub>2</sub> NSs<sup>234</sup> and MoS<sub>2</sub> decorated with Pt NPs<sup>235</sup> were reported. The Pt–MoS<sub>2</sub> sensor showed

a high and stable response% of 400 000% at 85% RH when tested over a few months.

Apart from the chemiresistor sensor, the optical, impedance, and capacitive sensors were employed for the detection of humidity. Luo *et al.*<sup>236</sup> and Li *et al.*<sup>138</sup> demonstrated all-fibre-optic humidity sensors comprising a WS<sub>2</sub> and MoS<sub>2</sub> film overlay on an SPF, respectively. They used a 1550 nm laser with SPF, which removes a portion of the cladding to form a polished region; propagated light confined in the core can escape out to this polished surface *via* evanescent waves, giving rise to strong interactions between light and the external environment. The responses of different types of fibre-optic humidity sensors are listed in Table 11. It is found that the MoS<sub>2</sub>-coated SPF sensor has a high response, and the MoS<sub>2</sub>-coated ESMF has a fast response time, which enables the fibre-optic sensor to monitor different breathing patterns of human beings. The impedance and capacitive humidity sensors are listed in Table 12. All of them show ultra-high sensing response, for instance, the sensing response of SmFeO<sub>3</sub>-modified MoS<sub>2</sub> nanocomposites is more than five orders of magnitude (10 598 100%) within the whole RH range of 11% to 95% RH at 10 Hz. Moreover, the combination of a polymeric material, poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS), and MoS<sub>2</sub> 2D NFKs gives a humidity sensor with an ultra-fast response and excellent recovery with values of 0.5 s and 0.8 s, respectively.

All the mentioned metal sulfide-based humidity sensors can work at room temperature, leading to wearable electronics applications. Among these four types of humidity sensors, fibre-

**Table 12** Comparison of different metal sulfide-based humidity sensors

| Material                                           | Structure       | Synthesis method               | Type       | RH range (%) | Response (%) or Sensitivity                         | $\tau_s/\tau_r$ | OT (°C) | Ref. |
|----------------------------------------------------|-----------------|--------------------------------|------------|--------------|-----------------------------------------------------|-----------------|---------|------|
| SnS                                                | Nanoflakes      | LPE                            | Resistive  | 3–99         | 2 491 000 (99% RH)                                  | 6 s/4 s         | RT      | 71   |
| WS <sub>2</sub>                                    | Thin film       | CVD                            | Resistive  | 25–90        | 235 600* (90% RH)                                   | ~5 s/~6 s       | RT      | 232  |
| ReS <sub>2</sub>                                   | Nanosheets      | CVD                            | Resistive  | 30–80        | 600 (70% RH)                                        | 20 s/10 s       | RT      | 234  |
| VS <sub>2</sub>                                    | Nanosheets      | LPE                            | Resistive  | 0–90         | 2900* (90% RH)                                      | 30–40 s/12–50 s | RT      | 233  |
| Pt–MoS <sub>2</sub>                                | NFKs            | Solution methods               | Resistive  | 35–85        | 400 000 (85% RH)                                    | 91.2 s/153.6 s  | RT      | 235  |
| TaS <sub>2</sub>                                   | Nanosheets      | CVD                            | Impedance  | 11–95        | 20 190 (11% RH)                                     | 0.6 s/2 s       | RT      | 238  |
| MoS <sub>2</sub>                                   | Nanospheres     | Hydrothermal method            | Capacitive | 17.2–89.5    | 81.9 pF/% RH (sensitivity)                          | 140 s/80 s      | RT      | 239  |
| MoS <sub>2</sub>                                   | QDs             | LPE                            | Impedance  | 10–95        | 2.21 MΩ/% RH (sensitivity)                          | 14 s            | RT      | 240  |
| MoS <sub>2</sub> /VS <sub>2</sub>                  | Nanocomposite   | Hydrothermal method            | Impedance  | 11–95        | 579 750* (95% RH)                                   | 23 s/13 s       | RT      | 35   |
| MoS <sub>2</sub> /ZnO                              | Nanocomposites  | Hydrothermal & chemical method | Impedance  | 11–95        | —                                                   | 1 s/20 s        | RT      | 241  |
| MoS <sub>2</sub> /Ag                               | Nanocomposites  | Mixture dispersion             | Capacitive | 11–97        | 21 112 pF/% RH (sensitivity)                        | ~1.5 s          | RT      | 242  |
| MoS <sub>2</sub> /SnO <sub>2</sub>                 | Nanocomposite   | Hydrothermal method            | Capacitive | 0–97         | 3 285 000 (97% RH)                                  | 5/13 s          | RT      | 243  |
| SmFeO <sub>3</sub> @MoS <sub>2</sub>               | Nanocomposites  | Hydrothermal method            | Impedance  | 11–95        | 10 598 100* (95% RH)                                | 1.5 s/29.8 s    | RT      | 244  |
| PEDOT:PSS/MoS <sub>2</sub>                         | Nanocomposites  | Exfoliation & deposition       | Impedance  | 0–80         | 50 kΩ/% RH, 850 Hz/% RH (sensitivity)               | 0.5 s/0.8 s     | RT      | 245  |
| SnS <sub>2</sub> /GO                               | Nanocomposites  | Solvothermal method, mixture   | Impedance  | 11–97        | 6 539 600 (97% RH)                                  | 0.9 s/10 s      | RT      | 246  |
| SnS <sub>2</sub> /TiO <sub>2</sub>                 | Nanohybrid film | LBL self-assembly              | Impedance  | 11–97        | 442 000 Ω/% RH (sensitivity)                        | <58 s           | RT      | 247  |
| SnS <sub>2</sub> /Zn <sub>2</sub> SnO <sub>4</sub> | Nanohybrid      | Solvothermal method            | Capacitive | 0–97         | 10 709 pF/% RH (sensitivity)                        | 18 s/1 s        | RT      | 248  |
| ZnO NDs/WS <sub>2</sub>                            | Heterostructure | Evaporation                    | Capacitive | 18–85        | 101.71 fF/% RH (sensitivity)                        | 74.51 s/25.67 s | RT      | 249  |
| WS <sub>2</sub> /SnO <sub>2</sub>                  | Nanocomposites  | LBL self-assembly              | Capacitive | 11–97        | 14 125 900 (97% RH)<br>21 112 pF/% RH (sensitivity) | 100 s/100 s     | RT      | 250  |



optic sensors have ultrafast response speed and low response and a complex measurement setup. However, it is necessary to find a way to easily integrate the fibre-optic sensor into one package that can be used for gas testing. Besides, humidity sensors can not only be used to monitor the patient's respiration profile continuously but also to determine the dehydration state. Highly sensitive and fast response and recovery humidity sensors are urgently required in real-world applications.

## 5. Summary and perspectives

This review shows a systematic summary of the crystal structure and gas sensing mechanism of metal sulfide nanomaterials, as well as the gas-sensing performance of metal sulfide-based devices. Here, to summarise the state-of-the-art metal sulfide gas sensors and analyse future and perspectives of the metal sulfide sensor market, we further provide a brief Strengths–Weaknesses–Opportunities–Threats (SWOT) analysis of metal sulfide technology for gas sensing.

### 5.1 Strengths

(1) Mechanism analysis. This is an efficient way to analyze and predict the gas sensing properties by combining theoretical (DFT) and experimental (*i.e.*, materials characterization and gas testing) methods. For instance, the higher the adsorption energy, the higher the selectivity toward this kind of gas molecule; the ELF plot can reflect the chemical bond between the gas molecule and metal sulfides, which affect the nature of physisorption and chemisorption and further influence the recovery time of the device; the charge transfer between the gases and metal sulfides can reveal the donor or acceptor of the gases, which is associated with the change of conductivity.

(2) Improvements in gas sensing performance.

(i) Functionalization of metal sulfides. To further improve the sensitivity, doping and defect substitution are the most commonly used tools in functionalization and are efficient methods to change the band structure, modify the electronic and transport properties, and enhance the gas sensing applications. However, most of the gas sensing behaviours of functionalized metal sulfides were analyzed through DFT calculations. There are a lack of experimental reports on the influence of defects on the metal sulfide-based devices' gas-sensing performance.

(ii) Schottky junction and heterojunction gas sensors. They are based on band alignment theory, which can significantly improve the gas sensing response and LOD. Most of them have excellent sensing performances, including high response, fast response time, wide detection range, and low LOD. Thus, more people are focusing on junction-based gas sensors.

(iii) FET gas sensors. Most FET gas sensors ultimately modify the sensitivity towards a target gas by changing the energy landscape of the sensor surface. This type of sensing device has been used to detect many types of gases, such as CO, NO, NH<sub>3</sub>, NO<sub>2</sub>, SO<sub>2</sub>, H<sub>2</sub>, and VOCs. However, most of the FET gas sensors are still not satisfactory in the aspects of device instability and

limited large-scale production, even though they have a fast response and selectivity.

(iv) Other sensing mechanisms. The optical gas sensor has been employed to detect non-polar gases, such as CH<sub>4</sub>, due to its high accuracy. Most of them are fibre optic gas sensors based on the reduction in the effective refractive index and showed high selectivity to methanol among VOCs. SAW gas sensors can detect a low concentration of NO<sub>2</sub> gas at room temperature with good efficiency and selectivity, and they are coated with polymers for the identification of breath biomarkers and the diagnosis of various diseases.

(3) Applications. Suitable applications for each type of gas sensor are found according to the specific gas-sensing performance of various metal sulfides. It is found that the IV–VI compound pristine metal sulfides, such as SnS, PbS, and GeS, show fast response and recovery time. The II–VI compound semiconductors, such as CdS and ZnS, have high response and selectivity to VOCs. However, most of their OTs are relatively high. Most of the transition metal sulfides have a larger electronegativity, potentially increasing the number of gas adsorption sites, and have been used for gas sensing of NO<sub>x</sub>, NH<sub>3</sub>, O<sub>2</sub>, and ethanol. With respect to VOCs, various pristine metal sulfides can be used for the detection of acetone, while functionalized or heterojunction-based metal sulfides are applied for sensing benzene, methane, formaldehyde, ethanol, and LPG. Most of them work at low temperatures, except for the detection of ethanol, whose OT is usually higher than 150 °C. In the aspect of inorganic gases, all types of metal sulfides are used for sensors. Heterojunction-based and FET-based metal sulfide devices are promising candidates for gas sensing. They can take advantage of metal sulfide and other materials (such as metal, dissimilar metal sulfide, metal oxide, and organic materials) as well as the field-effect induced by back gate bias. The large surface to volume ratio combined with significant changes in the measured signals upon gas adsorption induce high sensitivity and selectivity and low LOD. Besides, to improve their performance, researchers used light illumination to stimulate the charge transfer between the gas molecules and metal sulfide.<sup>251</sup> Thus, the light source can be integrated into the device in the future.

### 5.2 Weaknesses

(1) Lack of a low LOD. Biomarkers, such as NO<sub>x</sub>, NH<sub>3</sub>, and CH<sub>4</sub>, are at hundreds or tens of ppb in people. It is challenging to detect lung diseases, *i.e.*, asthma, by the detection of NO<sub>x</sub> in exhaled breath. MoS<sub>2</sub>/ZnO has the lowest LOD for NH<sub>3</sub>, which is 12 ppb. Au/Gr–MoS<sub>2</sub>–Gr/Au can detect 0.1 ppb NO<sub>2</sub>, and Ni-doped MoS<sub>2</sub> can detect 250 ppb SO<sub>2</sub>. For VOCs, α-Fe<sub>2</sub>O<sub>3</sub>/MoS<sub>2</sub> has a LOD of 1 ppm toward ethanol at room temperature. However, it is not as low as the LOD requirement for biomarker detection.

(2) Insufficient gas selectivity. Most gas testing reported in previous work was conducted in dry atmospheres. In contrast, the working environment may be under high humidity conditions in the real world; for instance, exhaled human breath contains almost saturated moisture; the RH level is higher in



the basin area. This thereby affects the sensitivity and selectivity of sensors. The effect of humidity could be reduced significantly by using a moisture absorber, increasing the OT, or optimizing the morphology or architecture of the materials. However, it is challenging to distinguish the specified concentration of the target gas in a mixture. For instance, the automobile exhaust pollutants primarily include CO, hydrocarbons, NO, SO<sub>2</sub>, particles (*i.e.*, some lead compounds, oil mist, and heavy metal compounds), and odour (*i.e.*, formaldehyde). The large-sized particles may cover the surface of the material and further affect the response to NO, CO, or SO<sub>2</sub>. Similarly, in the aspect of lung cancer detection, because there is no single biomarker for lung cancer, it is much more difficult than detecting asthma, diabetes, and halitosis. More work needs to be done in this field.

(3) Lack of reproducibility. 2D/nanostructured metal sulfides have large surface areas and abundant adsorption sites, which possess high adsorption energies towards gas molecules, especially chemisorbed gases. It is challenging to desorb them from the metal sulfides without external stimulation (high temperature, high bias voltage, or light illumination). Therefore, the devices could not be recovered to the initial state. Besides, the experimental conditions are hard to reproduce, and there are a lack of standardized methods to carry out the testing. Moreover, the absence of standardization, quality assurance, and reliable benchmarking are still crucial issues that hinder the applications of metal sulfides in the healthcare area.

(4) Lack of precise mechanism analysis. Most of the reported mechanisms are analyzed through DFT calculations. Sometimes, the simulation model cannot consider every detail shown in the experiment, which induces deviations between the simulation and experimental results. It is necessary to find an efficient tool or method to realize the benchmark.

All metal sulfide-based devices face the same problem as all solid-state sensors, such as translation from academic to industrial research, reproducibility of the lab conditions, batch production, integration/communication/power supply and real-world detection.

### 5.3 Opportunities

(1) New nanomaterials are emerging. Nanostructured metal sulfides with different forms, such as nanowires, nanoflowers, nanopores, and nanorods; or combined with hybrid materials, *e.g.*, materials decorated with metal or semiconductor particles, Schottky junctions with a metal layer or CNMs, and heterostructures with hBN, MXene, and MOFs; or those using novel substrates, such as PVP, PI, PDMS, and other flexible substrates, can help to realize skin patching of human beings or can be integrated into a textile.

(2) The matching between materials and circuit electrodes, such as the energy band and work function, needs to be considered in terms of device design. Meanwhile, real-time detection applications, signal processing, low energy consumption, intelligent operation, and integration with sensor networks (*e.g.*, internet of things) need to be considered. The

combinations of 2D gas sensors with artificial intelligence in smart cities, smart homes, and smart hospitals are hot topics for the future.

(3) FET devices can effectively improve the gas sensing performance, but it is necessary to control their energy consumption and turn-on voltage reasonably in the future. Device performance can be enhanced by designing the device structure (shape and size of gate-drain electrodes), selecting the dielectric layer, and selecting the substrate. Some metal sulfides (such as MoS<sub>2</sub> and WS<sub>2</sub>) could play an important role in electronics for logic, memory, and connections, enabling the extension of Moore's law,<sup>252</sup> as well as the Paradigm of "More than Moore".<sup>253,254</sup> There are primarily three challenges for these materials to meet industry needs in practical devices, such as the accuracy of the predicting properties, the methods of growing and testing high-quality materials, and the assessment of the device's performance.

### 5.4 Threats

The improvements of metal sulfide-based nanomaterials and other nanotechnologies in the gas-sensing performance are still being analyzed. The equipment used for the nanomaterial-based device should be different from those for traditional Si-based devices. For the future, the application of new nanomaterial devices still has a long way to go. For example, the current of the metal sulfide device is too small, and it is necessary to implement signal acquisition and intelligent control through a precise amplifier circuit. Defective materials are difficult to desorb, and additional UV light sources are needed to achieve rapid desorption, increasing the overall size and cost of the device. Time will be needed to reach market readiness and to overcome the reluctance to accept and introduce new technology, which now remains a severe hindrance in incorporating the production chain.

In this review, we listed the latest progress made in improving the field of 2D-metal sulfide-based gas sensors to overview the developments seen in this area extending from crystal features to device engineering. The crystal structures of metal sulfides and the gas sensing mechanism based on DFT analysis are introduced first. Various types of metal sulfide-based gas-sensing devices, including chemiresistors, functionalized-metal sulfides, Schottky diodes, heterojunctions, field-effect transistors, and optical, impedance, capacitive and SAW sensors, are compared and presented. We then discuss the extensive applications of metal sulfide-based sensors in gas sensing. Various gas sensors for the detection of VOC biomarkers (*e.g.*, acetone, benzene, methane, formaldehyde, and ethanol) and inorganic gases (*e.g.*, CO<sub>2</sub>, NH<sub>3</sub>, H<sub>2</sub>S, NO, and humidity) were discussed. There is a fabulous opportunity right now for developing 2D metal sulfides as gas sensors and use them for gas sensing, even integrated into the IoT system. However, they still have some shortcomings that need to be overcome, such as a high LOD, effect of a high humidity environment, insufficient gas selectivity, and low reproducibility in gas detection. It is necessary to develop new materials or construct advanced nanostructures to improve the





performances. Additionally, from a device architecture perspective, implementation of the new signal-processing technology and recognition algorithms based on a single-chip system using multiplex detection channels is a significant and promising route for the development of gas sensing platforms.

## Conflicts of interest

The authors declare no conflict of interest.

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