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Transition metal dichalcogenide based toxic gas sensing

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Abstract

Having affordable, power-lean, yet highly sensitive and selective gas sensors is essential to enable the widespread and continuous monitoring of air pollutant and toxic gases. In the last years the research community has identified two-dimensional transition metal dichalcogenides as gas sensitive nanomaterials with high potential for developing a new generation of room-temperature operated devices for trace detection in the ambient. This paper reviews the developments and achievements of the last few years, identifies current shortcomings where breakthroughs are most needed, and discusses aspects where research efforts should be put to overcome the main difficulties experienced. These efforts range from gaining more insight in the gas sensing mechanisms to ameliorating the synthesis of transition metal dichalcogenide nanomaterials for better controlling surface, interface and edge chemistry and defects.

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Keywords

Transition metal dichalcogenides, 2D nanomaterials, Chemoresistor, Field effect transistor gas sensor, Pollutant/toxic gases.

Introduction

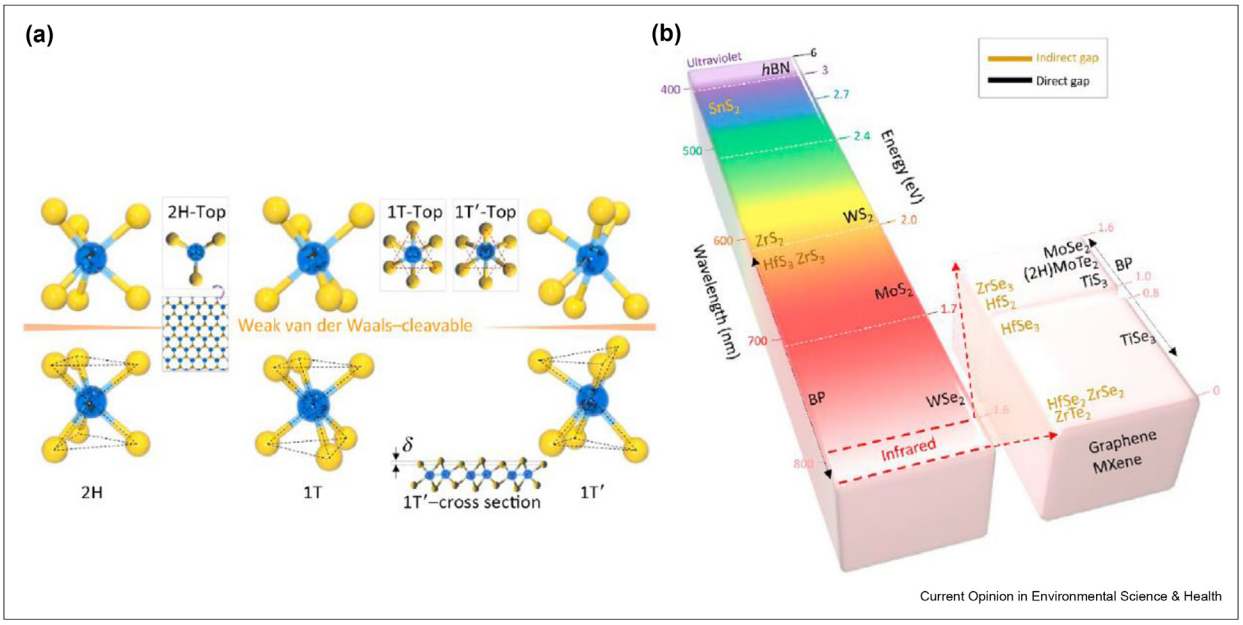
Among the main toxic gases and air pollutants we can find carbon monoxide, nitrogen oxides, ground-level ozone, volatile organic compounds, sulphur dioxide, ammonia vapours or hydrogen sulphide, only to cite a few. Most of these compounds, which are of anthropogenic nature, are responsible for 7 million premature deaths yearly, according to the WHO [1]. The development of gas sensors has known tremendous advances in terms of new sensing materials, size reduction, lowered power consumption and fabrication costs. Sensors are indispensable items in the monitoring of indoor/outdoor toxic gases and thus play an increasing role in environmental monitoring and air quality control. In the last few years, in a quest for achieving sensitive, ultra-low-power gas sensors, transition metal dichalcogenide (TMDC) nanomaterials have attracted the interest of the research community. This paper presents a critical mini review on the latest developments in TMDC gas sensors.

Semiconducting TMDCs have the general formula MX_2, where M = Mo, W and X = S or Se, with weak van der Waals bonding between layers and strong in-plane covalent bonding. They generally exhibit tuneable bandgaps that change from indirect (in bulk crystals) to direct (in monolayers), (see Figure 1). allowing applications, such as transistors, photodetectors, electroluminescent devices and, particularly, gas sensors [2]. TMDCs have appeal as gas sensing materials because they possess high surface-to-volume ratio, their electrical conduction properties are sensitive to their environment and, unlike standard metal oxides, TMDCs are able to operate at room temperature. Two-dimensional (2D) TMDCs (often referred to as monolayer TMDCs) show strong charge carrier confinement in the direction perpendicular to the 2D plane, making them very sensitive to any changes in their surface environment. The interaction between TMDCs and gas molecules generally involves a physisorption process accompanied by a moderate charge transfer between adsorbates and the TMDC. Despite being able to interact with different chemical species, group 6 TMDCs (most notably MoS_2, $MoSe_2$, $MoTe_2$, WS_2 and WSe_2) are fairly stable under ambient conditions, which makes them powerful platforms for the highly sensitive detection of gaseous species [3] (see Figure 2).

TMDC gas sensors: current status

The reproducible, reliable and affordable large-scale synthesis of TMDC thin films is a first prerequisite for the success of these nanomaterials in gas sensing applications. Additionally, their integration in transducing platforms for achieving gas sensors should be considered as well.

Figure 1



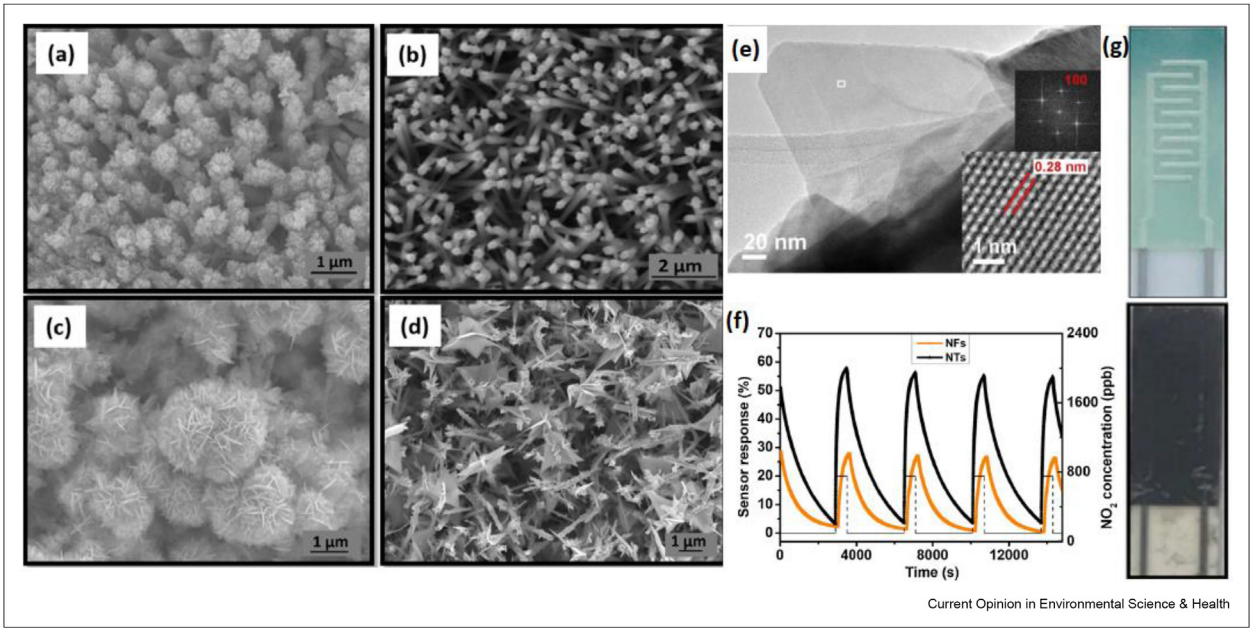
(**a**) Typical structures of layered transition metal dichalcogenides. Cleavable 2H, 1T and 1T0 structures in layered TMD are shown. (**b**) Bandgap of 2D layered materials varying from zero bandgap of graphene (white colour) to wide bandgap of hBN. The colour in the column is presenting the corresponding wavelength of bandgap, for example, the bandgap for MoS_2 (1.8 eV) is red colour and WS_2 (2.0 eV) is orange colour. Indirect materials are represented at left (SnS_2, ZrS_2, HfS_3, ZrS_3, $ZrSe_3$, HfS_2, $HfSe_3$, $HfSe_2$, $ZrSe_2$, and $ZrTe_2$) and direct bandgap materials are represented at right side of the column (h-BN, WS_2, MoS_2, WSe_2, $MoSe_2$, 2H-$MoTe_2$, TiS_3, and $TiSe_3$). 2D, Two-dimensional; hBN, hexagonal boron nitride; TMDs, transition metal dichalcogenides. Reproduced from Ref. [2], with permission ©Elsevier 2020.

TMDC synthesis routes

Initial studies on TMDCs used mechanically exfoliated single or multi-layered sheets. Despite this approach results in highly pure 2D TMDCs, it suffers from an inherent lack of scalability. An alternative for up-scaling the production of TMDCs is the liquid-phase exfoliation (LPE). This is a solution processing approach amenable to the additive manufacturing of gas sensors and thus, appealing for reducing the overall fabrication costs. However, the flakes obtained via LPE typically have small lateral dimensions and a distribution of layer thicknesses. Polycrystalline TMDC thin films exhibit low carrier mobilities, which negatively impacts device performance. Alternatively, continuous, large-scale TMDC films can be grown by techniques related to chemical vapor deposition (CVD). Films are grown on insulating substrates via the reaction of vaporized solid precursors or by the thermally assisted conversion of pre-deposited metal layers [4]. However, the quality of CVD-grown and LPE TMDCs is still lower than their mechanically exfoliated counterparts [5]. More recently, hydrothermal and solvothermal methods have been reported as alternatives for the low-temperature synthesis of 2D and 3D assemblies of TMDCs in large quantities.

Given the nature of the interaction with their chemical environment, most of the reported TMDC gas sensors employ either a chemoresistive or a field effect transistor (FET) transduction scheme. While FETs are more involved than chemoresistors, they can show higher sensitivity and stability. Under the chemoresisitve configuration a TMDC film coats interdigitated electrodes and changes in film resistance are monitored upon the exposure to gaseous species. The resistance in the 2D semiconductor nanomaterial can increase or decrease, depending on both the type of the semiconductor (p-type vs. n-type) and the gas (reducing vs. oxidising). Under a FET configuration, the TMDC film acts as the channel and metal contacts are used as source and drain. In FET gas sensors the bandgap of the TMDC is fundamental for enhancing sensitivity, which can be engineered via controlling the number of stacked layers [5]. Recent research efforts (see Table 1) have been centred on widening the spectrum of gases that TMDCs can detect and on ameliorating response intensity and dynamics. For doing so, the different approaches explored include modifying surface chemistry via playing with different morphologies, engineering chalcogen vacancies, loading TMDCs with noble metal nanoparticles, employing substitutional doping with suitable heteroatoms, designing metal oxide/TMDC hybrids or via using light-activated sensing [6]. Some examples of these strategies are discussed below.

Figure 2



SEM images of (**a**) WO_3 nanorods, (**b**) WO_3 nanoneedles, (**c**) WS_2 nanoflakes and (**d**) WS_2 nanotriangles. WO_3 nanomaterials are grown via the aerosol assisted CVD. WS_2 nanomaterials are obtained via the atmospheric pressure CVD (sulfurization) of WO3, (**e**) HRTEM image of a WS_2 nanoflake and corresponding FFT pattern, (**f**) WS_2 nanoflakes (orange), WS_2 nanotriangles (black) sensor responses (4 replicate response and recovery cycles) towards 800 ppb of NO_2 at the operating temperature of 150 °C, (**g**) Electrode area of the alumina transducer substrate coated with WO_3 nanomaterial (top, green colour), sulfurized to achieve WS_2 nanomaterial (bottom, black colour). Reproduced from Ref. [22], with permission © Elsevier 2021.

Recent advances in TMDC chemoresistive gas sensing

Kim [7] studied the effect of changing the electrode metal in the response of CVD-grown, 2D MoS_2 chemoresistors. The Schottky barrier height that develops at the electrode/TMDC interface enabled tuning selectivity to NO_2 (Al electrodes) or to CO_2 (Ag electrodes). Devices were operated at 60 °C in an inert (N_2) background. Lee and Choi [8] demonstrated NO_2 sensors on paper substrates using multiwalled carbon nanotubes (CNTs) and 2D TMDCs. Even tough sensors remained functional under crumpling, they hardly recovered their baseline and thus, important drift was experienced. Kim [9] studied p-type (WSe_2/WS_2) and n-type (MoS_2/WSe_2) white-light activated gas sensors. The former was selective to NO_2 and the later to NH_3 in a balance of N_2, however, the reasons for the observed selectivity are not completely understood. Light activation generates an excess of charge carriers that favours the adsorption of gas molecules [6,9]. Chen [10] reported $Ti_3C_2T_x/WSe_2$ nanohybrids for the detection of a variety of VOCs at room temperature. The hybrid sensor exhibited a remarkable ethanol sensitivity, but also a significant humidity cross-sensitivity. Similarly, Han and co-workers [11] reported the $SnS_2/Ti_3C_2T_x$ hybrid for detecting trimethylamine vapours. The enhancement in sensitivity to VOCs was attributed to the heterojunction interfaces formed by the MXene/TMDC nanohybrids. Furthermore, the hybridization of MXenes with TMDCs helps overcoming the instability and oxidization tendency of individual MXenes. Li [12] fabricated a gas sensor using few-layer WSe_2 nanosheets and demonstrated the room-temperature detection of dimethyl methyl phosphonate, yet at far too high concentrations. Wang [13] demonstrated a visible-light activated gas sensor based on MoS2/rGO, enabling the detection of HCHO. The enhanced HCHO sensing was attributed to the visible-light photocatalytic activity of MoS_2 combined to the efficient charge separation of rGO. However, the sensor was cross-responsive to ammonia, alcohols and ambient moisture. The reader is referred to Ref. [6] for an updated account on MoS_2 based materials aimed at detecting VOCs (e.g., ethanol, methanol, formaldehyde or benzene). Han [14] developed a surface functionalization strategy, where WO_3 nanosheets were aligned on the surface of WS_2 nanoflakes via a sonochemical method. The hybrid exhibited high NO_2 sensitivity, resilience to ambient humidity, improved response time and long-term stability. These characteristics were attributed to a strong interlayer electronic coupling, and the p–n heterojunctions formed. Kang [15] investigated the ammonia sensing properties of VS_2 nanosheets (NSs) Even though affected by moisture levels, when operated at 40 °C, VS_2 NSs exhibit high selectivity to ammonia, which adsorbs at edge sites and transfers electronic charge to the p-type VS_2 NSs.

Table 1

Recent developments and results in transition metal dichalcogenide gas sensors.

Material	Synthesis	Transducing scheme	Target Gas	Range	LOD	Response intensity	Response time	Selectivity	Stability test	Humidity	Operating Conditions	Ref
2D WS2	Liquid phase exfoliation	Cata-luminescence	H2S	0.3–6 ppm	N/A	10,000 @ 5 ppm	ms	Yes	1 week	N/A	187 °C	[38]
CNT + Ws2 or MoS2	Commercially available	Chemoresistor	NO2	0.1–10 ppm	0.1 ppm	10 % @ 2 ppm	Tens of min to hours	Yes	N/A	N/A	150 °C	[8]
Schottky contact + MoS2	CVD	Chemoresistor	NO2 (Al); CO + CO2 (Ag)	10 ppm	N/A	80 % @ 10 ppm	Tens of min	No	N/A	20 % constant	60 °C Measured in N2 background	[7]
WSe2/WS2 MoS2/WSe2	CVD and ALD	Chemoresistor	NO2 and NH3	50–500 ppm	N/A	150 % @ 500 ppm NH3 300 % @ 500 ppm NO2	Tens of min	Yes	N/A	N/A	RT and white light activation N2 background	[9]
Ti3C2Tx/WSe2	Liquid phase exfoliation	Chemoresistor	EtOH	1–40 ppm	N/A	9 % @40 ppm	Sec	No (alcohols, aromatics)	30 days	Response drops by 50 % when moisture changes from dry to 80 % RH	RT	[10]
WSe2	Liquid phase exfoliation	Chemoresistor	DMMP	10–500 ppm	10 ppm	8.91 % @10 ppm	Tens of min	Yes, VOCs and water, NO2 or NH3 not tested.	7 weeks	N/A	RT	[12]
MoS2/rGO	Hydrothermal	Chemoresistor	HCHO	1–50 ppm	N/A	64 % @10 ppm	Sec to min	No (alcohols, ammonia)	90 days	Response drops with moisture level	RT + visible light	[13]
WS2–WO3	Mechanical exfoliation	Chemoresistor	NO2	0.05–5 ppm	N/A	16 % @5 ppm	Sec to min	N/A	6 months	Resilient	RT	[14]
VS2	Liqui phase exfoliation	Chemoresistor	NH3	1–10 ppm	N/A	257 % @ 10 ppm	Tens of min	N/A	2 weeks	Response drops with moisture level	40 °C	[15]
ZnO NRs/WS2	Liquid phase exfoliation and microwave-irradiation-assisted solvothermal	Chemoresistor	H2S	0.1–5 ppm	N/A	100 % @ 3 ppm	Sec to min	Yes	6 months	Slight drop in response in humid conditions	250 °C	[16]
Flower WS2	Chemical vapour transport	Chemoresistor	H2S	10–150 ppm	N/A	153 % @ 50 ppm	Sec to min	No, SOF2, SO2, SO2F2	N/A	N/A	200 °C	[17]
WS2	Liquid phase exfoliation	Chemoresistor	NO2	2–10 ppm	N/A	27 % @ 10 ppm	Sec to min	Cross-responsive to NH3	N/A	N/A	RT	[18]
WS2/SnO2	Liquid phase exfoliation	Chemoresistor	NO2	0.5–20 ppm	N/A	400 % @ 5 ppm	Sec to min	Cross-responsive to EtOH	30 days	Resilient. 25 % drop for 0 to 80%RH	RT, UV light	[19]
WS2/WO3	Hydrothermal	Chemoresistor	NO2	2–50 ppm	1 ppm	6600 % @ 10 ppm	Tens of min to hours	Not responding to H2 nor CO	N/A	N/A	200 °C	[28]
Au–MoS2	Hydrothermal	Chemoresistor	CO	N/A	N/A	20 % @ 10 ppm	Tens of min to hours	N/A	N/A	N/A	RT	[22]
Co–Zn doped MoS2/graphite	Wet chemistry synthesis of Zn and Co NPs and impregnation onto commercial MoS2 powders	Chemoresistor	NO2	0.05–5 ppm	6.2 ppb	60 % @ 1 ppm	Min	Cross-sensitive to NH3	50 days	Affected by humidity for high moisture levels	RT	[23]
WS2–SnO2 QDs	Liquid phase exfoliation	Chemoresistor	NH3	0.1–10 ppm	10 ppb	850 % @ 10 ppm	Tens of min to hours	Ten times lower response to NO2	8 weeks	N/A	RT blue light	[24]
WS2	CVD	Chemoresistor	NO2	0.05–0.8 ppm	5 ppb	5500 % @ 0,8 ppm	Min	Cross-responsive to H2S	8 months	50 % drop or response at 50 % RH	150 °C	[25]
Pd-WS2 or Pt-WS2	CVD	Chemoresistor	H2	10–1000 ppm	5 ppb	30 % @ 100 ppm	Min	Cross-responsive to NO2	6 weeks	Resilient to humidity	150 °C and RT	[26]
Cu2O-WS2	CVD	Chemoresistor	H2S	40 ppm	34 ppb	138 % @ 40 ppm	Min	Selective	7 months	Resilient to humidity	RT	[27]
MoS2	CVD	Chemoresistor	NO2 NH3	0.02–0.8 ppm 2–10 ppm	5 ppb 100 ppb	65 % @0.8 ppm 11 % @ 10 ppm	Sec to min	Dually selective via oper temp	3 months	Resilient to humidity	100 °C RT	[28]
WSe2	CVD	Chemoresistor	NO2 NH4	0.02–0.8 ppm 2–10 ppm	100 ppb 1 ppm	20 % @0.8 ppm 16 % @ 10 ppm	Min	Dually selective via oper temp	4 months	Resilient to humidity	100 °C 150 °C	[29]
ReS2	Colloidal synthesis	Electrochemical	NH3	20,000 ppm	NA	3500 % @20,000 ppm	Sec to min	No (water, o2, …)	N/A	Cross-sensitive	RT Measured in N2 background	[36]

MoS2/ZnO	Microwave-hydrothermal	Optical	NO2	10–200 ppb	0.1 ppb	226 % @ 0,2 ppm	Sec to min	N/A	N/A	34 % decrease in 80 % humid air	RT and NIR excitation	[37]
WS2/IGZO	CVD and PMMA stamp transfer	Transistor	NO2	1–300 ppm	30 ppb	30,000 % @10 ppm	Tens of min	N/A	N/A	N/A	RT	[31]
1T/2H heterophase MoS2	Li-ion intercalation exfoliation	Transistor	NO2	0.025–10 ppm	25 ppb	25 % @2 ppm	sec to min	YES	N/A	N/A	RT	[32]
WS2/GeSe/WS2	Mechanical exfoliation and multiple transfers of flakes using dry transfer method	Transistor	NH3	25–200 ppm	N/A	9 % @ 25 ppm	ms	No	N/A	N/A	RT and red light. Measured in vacuum	[33]
Re0.5Nb0.5S2	Chemical vapour transport	Transistor	NO2	0.05–15 ppm	N/A	32 % @ 1 ppm	Tens of min	Yes	N/A	40 % high response increase to NO2	RT	[34]
PdSe2	CVD	Transistor	NO2	0.1–5 ppm	100 ppb	18 % @1 ppm	Tens of min to hours	Yes	4 months	N/A	RT	[35]

N/A: Not available. Unless otherwise specified, all sensors tested under dry air conditions.

Sakhuja [16] reported a TMDC–metal oxide heterostructure for the selective detection of H_2S. WS_2 nanosheets, obtained by LPE were used as the seed for fabricating the nano heterostructures with in-situ, solvothermal grown ZnO nanorods. This creates active sites at the basal plane of WS_2, which is otherwise inert to H_2S, thus achieving selectivity to H_2S among other species such as NH_3, SO_2 or NO_2 at an operating temperature of 250 °C. Chen [17] reported a flower-likeWS_2 nanostructure operated at 200 °C for detecting products of SF_6 decomposition. First-principles results indicated that the adsorption at WS_2 edge structures and associated electron transfer were responsible for the response observed. Patrick [18] reported that room temperature operated LPE WS_2 nanosheets showed good response towards NO_2 with NH_3 cross-sensitivity. Xia [19] used SnO_2 quantum dots (QDs) decorated on the surface of few layer WS_2 nanosheets to form 2D/0D heterostructures via a solution process and self-assembly method. The heterostructures showed enhanced response to NO_2 and fast response/recovery rates. This performance was attributed to the efficient interfacial charge separation achieved via the 2D/0D heterostructures under ultraviolet illumination. Barbosa [20] reported the preparation of WS_2/WO_3 heterostructures for the development of nitrogen dioxide (NO_2) sensors via a hydrothermal route achieving WS_2 nanosheets deposited over the tungsten oxide phase. Similarly, Abun and co-workers [21] synthesized $MoSe_2$/ZnO hybrids for detecting H_2. In TMDC/metal oxide hybrids, an electronic sensitization mechanism based on the electronic barriers introduced by the p-n semiconductor junctions operated above room temperature explains the enhancement achieved. Rawat [22] reported a hydrothermal approach to synthesize hybrid Au–MoS_2 nanoflowers. Au nanoparticles were deposited over MoS_2 by evaporation, achieving remarkable room-temperature response towards CO. Fan [23] presented a structure of dispersed Co and Zn atoms doped on a MoS_2/graphite. This composite showed high responses toward NO_2 at room temperature, and low cross-sensitivity to NO, NH_3, H_2, CO, and ethanol. The gas-sensing mechanism can be attributed to the chemical sensitization brought about by Co. Shrama [24] used 2D WS_2 nanosheets decorated with SnO_2 QDs for detecting NH_3 vapours. Operated at room temperature, this hybrid was able to detect ammonia down to ppb levels when under blue-light illumination. Alagh [25] reported the synthesis of 2D layered WS_2 nanosheets assembled on 1D WS_2 nanostructures by combining the aerosol assisted CVD and atmospheric pressure CVD, for detecting NO_2. Sensors show stable and reproducible responses towards NO_2 at ppb levels with moderate NH_3 and moisture cross-sensitivity. This strategy has been explored further for achieving WS_2 nanoflakes loaded with PtO, PdO [26] or Cu_2O [27] for selectively detecting NO_2 and H_2S, respectively. Anannouch [28] reported the CVD growth of 3D assemblies of MoS_2 nanosheets, which showed

dual selectivity towards NH_3 (at room temperature) and to NO_2 (at 100 °C) and very small humidity cross-sensitivity. Alagh [29] developed 2D WSe_2, by the selenization of tungsten trioxide (WO_3) nanowires. Their selectivity could be tuned by setting its operating temperature (150 °C for NH_3 and 100 °C for NO_2). WSe_2 under dark or UV light activation has been found to be remarkably sensitive to triethylamine vapours, yet suffering from important cross-sensitivity to NH_3 and NO_2 [30].

Recent advances in TMDC transistor gas sensing

Tang [31] studied the gas-sensing performance of CVD-WS_2/IGZO transistors and demonstrated excellent gas selectivity toward NO_2. The superior gas-sensing performance was attributed to the doping effects of NO_2 on the heterojunction and the modulated Schottky barrier value at the interfaces of WS_2/IGZO/metal contacts. However, devices exhibited long recovery times. Zong [32] used a thermal annealing process to tune 1T/2H (i.e., metal/semiconductor) phase fractions in lithium-intercalated MoS_2. 1T/2H heterophase MoS_2 transistors show a p-type semiconducting characteristic and significantly enhanced sensitivity and selectivity to NO_2 at room temperature. Afzal [33] designed a compact vertically stacked 2D n-WS_2/p-GeSe/n-WS_2 heterojunction bipolar transistor gas sensor. The device was fabricated via mechanical exfoliation and PDMS stamp transfer. Performance was investigated in the detection of NH_3 and O_2 at room temperature under vacuum and visible light illumination, achieving ultrafast response dynamics (ms). The enhanced response observed in TMDC hybrid transistors is attributed to the defects and extra adsorption sites appearing at the heterojunction interfaces [32,33]. Azizi [34] demonstrated a room-temperature gas sensor using few-layer $Re_{0.5}Nb_{0.5}S_2$. The sensing transistor exhibits thickness-dependent carrier type, and upon exposure to NO_2 molecules, its electrical resistance considerably increases or decreases depending on the number of layers. The sensor is selective to NO_2 with only minimal response to other gases such as NH_3, CH_2O, and CO_2. In Ref. [35], Fan synthesized 2D $PdSe_2$ nanofilms with thicknesses ranging from 2 to 28 nm on Si in a transistor configuration. An 8 nm-thick PdSe2/Si transistor was found selective toward NO_2 and barely responsive to NO, H_2, CO, NH_3, or C_2H_5OH. Fist-principles studies revealed that the sensing mechanism relies on adsorption and charge transfer between NO_2 and the $PdSe_2$ surface.

Other transducing platforms

Besides chemoresistive and FET transducing schemes, a few groups have reported alternative approaches for TMDC gas sensing. Martín-García [36] studied drop-casted colloidal suspensions of ReS_2 contacted with Au for their electrochemical gas sensing properties while operated at room temperature. They were found sensitive to NH_3, with remarkably fast response dynamics in the range of few seconds. However, they suffered from an important cross-sensitivity to ethanol, acetone and water vapour. By performing ligand exchange processes the electronic properties and reactivity of the material were tuned to ameliorate selectivity. Xia [37] proposed a room temperature optoelectronic NO_2 sensor based on sulphur-vacancy enriched, hydrothermally-grown MoS_2 (SV−MoS_2). Sensors exhibited enhanced sensitivity to ppb levels of NO_2 under NIR illumination at room temperature. In addition, through functionalization with ZnO QDs, the SVMoS_2/ZnO nanocomposites exhibited further enhancement in responses and response/recovery rates. This was due to the improved charge generation and transfer induced by sulphur vacancies under NIR. Zhou [38] used LPE WS_2 nanosheets, for constructing cataluminescent (CTL) H_2S gas sensors operated at 187 °C, with 200 ms response time. WS_2 nanosheets had larger surface, richer edges and more sulphur defects than bulk WS_2. When exposed to air, WO_3 was generated forming WS_2/WO_3, and WO_3 could keep balance with WS_2 during H_2S exposure due to a reversible S−O bonding exchange.

Main challenges and how to address them

Despite the research efforts and results achieved, there are still important challenges to be addressed before TMDC gas sensors can make their potential market opportunities. Their electrical properties are known to be highly sensitive to extrinsic effects that arise from surfaces and interfaces such as metal contacts, dielectric interfaces and defects. These unintentional extrinsic effects often obscure the intrinsic electrical response of TMDCs and this lack of systematic understanding should be addressed by studying further the physics and chemistry in material synthesis and sensor design for practical applications [39]. While TMDCs hold promise for detecting NO_2 and NH_3, their sensitivity and selectivity towards other pollutant/toxic gases still needs to be enhanced. First-principles studies suggest addressing this via doping 2D TMDCs with heteroatoms such as P or Se doping of $MoTe_2$ for detecting CO [40] and HCL [41], respectively. Similarly, the doping with Au, Ag, Pt, Pd and Ni has been explored as well for tuning selectivity of $MoTe_2$ [42] and P-doping of MoS_2 for enhancing NH_3 detection [43]. A different approach consists of exploring alternative TMDCs such as 1T-$HfTe_2$ [44] or PtTeS [45] for detecting NO or Janus MoSSe and MoSTe for detecting polar molecules such as acetone [46,47]. MoS_2 and $MoSe_2$ thin films exposed to strong electron-donor gaseous analytes undergo a semiconductor−metal 2H-1T TMDC phase transition [48], which could be exploited for boosting sensor response. Additionally, surface functionalization with molecules or nanomaterials, especially through the covalent attachment of thiolated molecules on the sulphur vacancies or via changing the organic compounds in the

liquid phase exfoliation of TMDs [49] would help tuning selectivity. While room temperature operation is an asset of TMDCs towards ultralow power gas sensing, response and recovery dynamics are often far too slow for practical applications. This could be addressed via edge and defect engineering in TMDCs, as a way to tailor surface chemistry and gas adsorption properties. First-principles studies and operando near ambient pressure X-ray spectroscopy indicate that edges and chalcogen vacancies are highly reactive for gas adsorption and enhanced charge transfer [50–54]. TMDCs are prone to suffer from oxidation when exposed to the ambient and this eventually impacts negatively the long-term stability of gas sensors. Recently, noble transition metal dichalcogenides have been introduced for achieving gas sensors with enhanced air stability under normal operation conditions [55]. TMDC gas sensor research is still at an early stage if compared to the one conducted for metal oxides (MOXs) [56] and it is still unclear whether TMDCs will find some niche gas sensing applications, thus displacing MOX sensors or, instead, will remain as an *ingredient* for developing hybrid nanomaterials with enhanced sensing performance.

Concluding remarks

The field of gas sensors based on 2D-TMDCs is fast-evolving and research is directed both to gain a better understanding of the physicochemical phenomena governing response, and to enhance further the sensitivity, selectivity and long-term stability experienced. While operando spectroscopies can help to advance the former, the later aspects can be addressed via ameliorating synthesis and post-synthesis methods, thus enabling the engineering of surfaces, edges and defects in TMDCs and hybrids.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data were used for the research described in the article.

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