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Synthesis of MoS₂-based nanostructures and their applications in rechargeable ion batteries, catalysts and gas sensors: a review

Wei Sun, ^{Dac} Yaofang Zhang, *ac Weimin Kang, ^{Dad} Nanping Deng, ad Xiaoxiao Wang, ad Xiaoxing Kang, ac Zirui Yan, ac Yingwen Panac and Jian Nib

Molybdenum disulfide (MoS₂) is a two-dimensional (2D) layered material with a graphene-like structure that has attracted attention because of its large specific surface area and abundant active sites. In addition, the compounding of MoS_2 with other materials can enhance the performance in applications such as batteries, catalysts, and optoelectronic devices, *etc.* MoS_2 is prepared by various methods, among which chemical deposition and hydrothermal methods are widely used. In this review, we focus on summarizing the applications of MoS_2 and MoS_2 composite nanomaterials in rechargeable ion batteries, catalysts for water splitting and gas sensors, and briefly outline the preparation methods.

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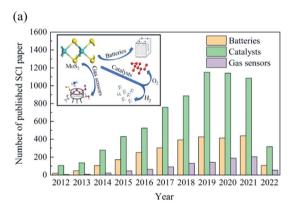
1. Introduction

Nanomaterials have attracted increasing research interest as a result of its fascinating physicochemical properties, such as the nano-size effect and large specific surface area. In 2005, the emergence of monolayer graphene set off a research boom in 2D materials. Many novel 2D materials have also been developed, such as hexagonal boron nitride (hBN) and transition metal dichalcogenides (TMDs). They are widely used in energy, sensing and other applications due to their excellent physical and chemical properties. MoS₂, a member of TMDs, is a promising 2D material among compounds with graphene-like structures.

It is well known that MoS₂ materials have a wide range of applications, and we found that it has a high proportion of catalysts, batteries and gas sensors applications by searching the Web of Science for articles related to the applications of MoS₂ in the last decade (Fig. 1b). Fig. 1a summarizes the number of published SCI papers on MoS₂ over the last decade (up to May 2022) in the batteries, catalysts, and gas sensors. It is clear that MoS₂ is attracting more and more attention in these applications.

MoS₂ exhibits unique advantages over graphene-based or hBN-based nanomaterials in these applications. In detail, in

batteries, MoS₂ is used as an electrode material due to its high specific surface area and unique layer-like structure. ¹⁰ In catalysts, MoS₂ is a promising alternative to the precious metal Pt catalysts for hydrogen reaction evolution (HER) and



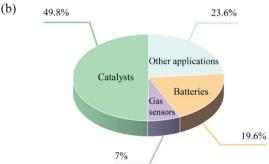


Fig. 1 (a) Statistics of MoS_2 core publications in batteries, catalysts, and gas sensors. (b) Percentage of core publications of MoS_2 in different applications in the last decade (up to May 2022).

^aState Key Laboratory of Separation Membranes and Membrane Processes, Tiangong University, Tianjin 300387, PR China

^bDepartment of Electronic Science and Technology, College of Electronic Information and Optical Engineering, Nankai University, Tianjin, 300350, China

School of Physical Science and Technology, Tiangong University, Tianjin 300387, PR China

^dSchool of Textile Science and Engineering, Tiangong University, Tianjin 300387, China

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photocatalytic water splitting, while MoS₂ can be used in combination with other materials to improve visible light catalytic activity for the degradation of organic pollutants in industrial wastewater.^{11,12} In terms of gas-sensitive properties,

catalytic activity for the degradation of organic pollutants in industrial wastewater.^{11,12} In terms of gas-sensitive properties, MoS₂ has good responsiveness and selectivity to some gases at room temperature (RT), which has led to widespread research and application of MoS₂ materials in gas sensors.¹³

Recent years, many reviews about MoS₂ nanomaterials were published. Some researchers have reviewed the application and preparation of MoS₂ in energy (such as batteries and catalysts), ^{14–16} some have reviewed the application and preparation of MoS₂ in electronic components (such as memristors and field-effect transistors), ^{17–20} some focus on MoS₂ for detection and sensing applications, ^{21–23} some have listed in detail the synthesis and application of 1T MoS₂, ^{24–26} and others have focused on the synthesis method of MoS₂. ²⁷ Based on the previous researches and summaries, in this review, we comprehensively and systematically describe the applications of MoS₂ and MoS₂-based composites in rechargeable ion batteries, catalysts and gas sensors in recent years, and summarize the corresponding preparation schemes.

2. Applications and synthesis strategies of MoS₂ in rechargeable ion batteries

To meet future energy storage needs, rechargeable ion batteries based on Li⁺, Na⁺, Al³⁺ and Zn²⁺ have been widely studied and prepared.²⁸⁻³¹ MoS₂ has a layered structure, which are connected by van der Waals forces with weak interlayer interactions and large layer spacing.³² High theoretical capacity, high charging rate and excellent stability make MoS₂ become a promising electrode material. In this work, we will focus on the application and preparation of MoS₂ as electrode materials.

2.1 Lithium-ion batteries

Using MoS₂ or composites of MoS₂ for the anode materials is beneficial to lithium-ion batteries (LIBs). Wei *et al.* ³³ studied the electrochemical reactions of MoS₂ nanosheets in LIBs. Their study represented that intercalation of Li ions into MoS₂ anode contributes the electrochemical charge storage. However, the low conductive of MoS₂ and its aggregation during the electrode manufacturing process greatly hinder the development of LIBs. ^{34,35} In order to improve the performance of MoS₂ as an electrode material for LIBs, there are two main options, one is to change the structure of MoS₂ material, and the other is to prepare MoS₂ composites.

On the one hand, Zhao *et al.*³⁶ studied MoS₂ materials with nanotube structures to improve electrochemical performance. They reported a facile wet etching method for the preparation of low crystalline MoS₂ nanotubes. First, MoO₃ nanobelts (MoO₃ NBs) were prepared by hydrothermal method. Sodium molybdate dihydrate (Na₂MoO₄·2H₂O) and nitric acid were used in this step. Second, 3D MoS₂ nanomasks were grown *in situ* on MoO₃ NBs, which was obtained by the chemical reaction of sublimed sulfur with MoO₃ NBs in CVD quartz tube. Finally,

 MoS_2 nanotubes (MoS_2 NTs) were synthesized by mixing the previously obtained MoO_x/MoS_2 NBs with concentrated hydrochloric acid. As demonstrated in Fig. 2a, the inner MoO_x are etched with concentrated hydrochloric acids to yield low crystalline MoS_2 NTs. With the increase of etching times, the molybdenum oxide is gradually removed which allowed the internal cavity of MoS_2 NTs to be emptied. After the fourth etching process, most of the molybdenum oxides were removed to give MoS_2 NTs (Fig. 2b).

The electrochemical test results illustrated that MoS_2 NTs, as the anode material for LIBs, reached a specific capacity of 1253 mA $\rm g^{-1}$ at a current rate of 200 mA $\rm g^{-1}$ and was stabilized after 250 cycles. Obviously, the low crystalline MoS_2 NTs have even higher specific capacity and cyclic performance than the reported electrode materials. 37,38

On the other hand, some researchers have investigated MoS₂ nanocomposites to improve the electrochemical properties of MoS₂ in LIBs.

Wu *et al.*³⁴ reported an electrode material of two-layer carbon-coated MoS₂/carbon nanofiber (MoS₂/C/C fiber) which prepared by hydrothermal and electrospinning method. First, MoS₂ spheres were obtained by hydrothermal. Hexaammonium heptamolybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O), thiourea (NH₂CSNH₂), and polyvinylpyrrolidone (PVP) were used in this step. Second, MoS₂/C spheres were fabricated by using glucose and the above-obtained MoS₂ spheres. Finally, they synthesized MoS₂/C/C nanofiber by electrospinning method. Polyacrylonitrile (PAN), *N*,*N*-dimethylformamide (DMF) and the above obtained MoS₂/C spheres were used. The preparation process of MoS₂/C/C fiber is shown in Fig. 2c.

Meanwhile, Zhang et al. 35 synthesized ${\rm TiO_2/C/MoS_2}$ microspheres as anodes for LIBs. ${\rm TiO_2/C/MoS_2}$ microspheres were prepared by solvent-thermal method and calcination. First of all they used PVP, acetic acid and tetrabutyltitanate (TBT) in a Teflon-lined autoclave for the reaction to prepare ${\rm TiO_2/C}$ materials. Secondly, ${\rm TiO_2/C/MoS_2}$ was synthesized by the obtained ${\rm TiO_2/C}$, ammonium molybdatetetrahydrate ((NH₄)₆-Mo₇O₂₄·4H₂O) and thiourea (CH₄N₂S). The preparation process of ${\rm TiO_2/C/MoS_2}$ microsphere is shown in Fig. 2e.

No matter MoS₂ is compounded with carbon materials or TiO₂ materials, the electrochemical properties of MoS₂ materials have been improved. On the one hand, for the MoS₂/C/C electrode, the double-layer carbon coating (Fig. 2d) could not only suppress the irreversible reaction, but also confine the volume change during the lithiation/delithiation process.³⁴ Moreover, MoS₂/C/C fiber has better cycling performance than MoS₂ spheres (Fig. 2g). On the other hand, the unique structure with flower-shaped of TiO₂/C/MoS₂ (Fig. 2f) could not only enlarge the electrolyte–electrode interface area but also shorten the diffusion length of Li⁺ intercalation/deintercalation.³⁵ Compared with MoS₂ materials, the cycling performance of TiO₂/C/MoS₂ are enhanced (Fig. 2h).

2.2 Sodium-ion batteries

Sodium ion batteries (SIBs) are considered as an alternative to LIBs because of their abundant reserves and low cost. However,

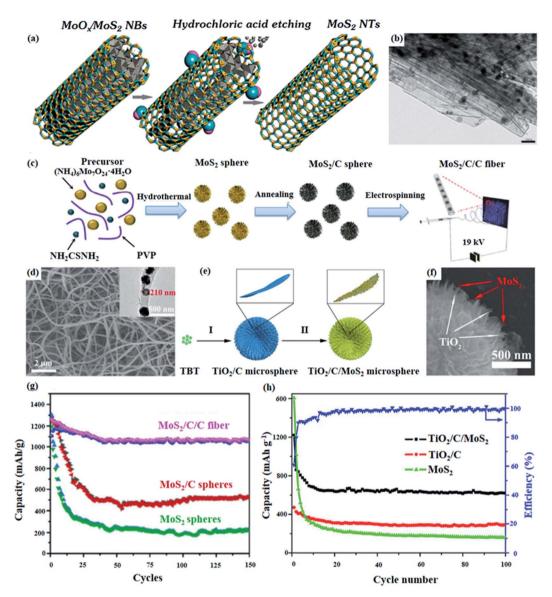


Fig. 2 (a) MoS_2 NTs are obtained after etching MoO_x/MoS_2 NBs with concentrated hydrochloric acid. (b) MoS_2 NTs obtained from the fourth etching. (c) Schematic illustration of the preparation process of $MoS_2/C/C$ fiber. (d) SEM images of $MoS_2/C/C$ fiber. The inset is a magnified TEM image of the sample. (e) Schematic diagram of the synthesis of $TiO_2/C/MoS_2$ microsphere. (f) SEM images of $TiO_2/C/MoS_2$ microsphere. (g) Capacity retention of the MoS_2 , MoS_2/C , and $MoS_2/C/C$ fiber electrodes at a current density of 0.2 A g⁻¹ for the subsequent 150 cycles. (h) Comparative cycling performance of MoS_2 , TiO_2/C and the $TiO_2/C/MoS_2$ microsphere at a current density of 100 mA g⁻¹. (5)

Na⁺ has larger radius than Li⁺,³⁹ which hingers the development of SIBs. As a highly promising electrode material, MoS₂ has not only a layered structure but also a large interlayer spacing, which promises to solve the inherent defects of SIBs. However, MoS₂ also has inherent limitations, such as low intrinsic electron conductivity. In response to these characteristics, some researchers have prepared composites of MoS₂ ^{40–43} and others have improved the structure of MoS₂ by doping or inserting molecules to achieve improved electrochemical properties.^{40–45}

Pan *et al.*⁴² reported a simple template method to prepared MoS_2 /amorphous carbon (C) microtubes (MTs) composed of heterostructured MoS_2 /C nanosheets. The synthesis of MoS_2 /C MTs was achieved by a three-step procedure: first, obtaining Sb_2S_3 microrods by a simple hydrothermal method, second,

 MoS_2/C nanosheets were grown on the outer surface of Sb_2S_3 microrods by using sodium molybdate dehydrate (Na_2MoO_4 - $\cdot 2H_2O$), N_2H_4CS , and glucose ($C_6H_{12}O_6$) in a Teflon-lined stainless steel autoclave for chemical reaction, and third, MoS_2/C MTs were obtained by removing Sb_2S_3 microrods via annealing. The synthesis schematic is shown in Fig. 3a. Electrochemical measurements demonstrated that MoS_2/C MTs possessed high specific capacity and excellent stability, improving the electrochemical performance of SIBs.

Similarly, some researchers have also reported composites of MoS₂ for enhancing the electrochemical performance of SIBs.

The MoS₂/carbon nanofibers (MoS₂/CNFs) were prepared by a two-step procedures: first, obtaining ammonium tetrathiomolybdate (AMT), and second, synthesizing MoS₂/CNFs by

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(a) Hydrothrtmal Calcination Ar+H, Sb_2S_3 Sb₂S₃@MoS₂/C MoS₂/C microrod microrod microtube Thiourea, Glucose Ar/H₂, 700°C IPA/H₂O Acid pickling 200°C,12h (d) Hydrothermal Selenization 0.66 nm 0.62 nm 10 µm MoS2-Se, MoS, MoS, Mo Se 600 600 Interlayer distance increased Conductivity increased 500 500 capacity (mAh g-1) capacity (mAh g-1) 50 mA g-1 50 mA g-1 400 400 300 300 200 200 100 100 ERRYAMES DMA.NOS? BRRY MOST DAIL MOST (g) from 0.62 nm to 1.26 nm

Fig. 3 (a) Schematic illustration of the synthesis process of MoS_2/C MTs.⁴² (b) Schematic diagram of the fabrication process of MoS_2-C hollow rhomboids. 41 (c) FESEM images of OMSCF calcined in air at 400 °C (OMSCF-400). 43 (d) Schematic illustration of the synthesis of MoS_{2-x}Se_x/G. 45 (e) Capacity of all intercalated MoS₂ at 50 mA g⁻¹ arranged according to the interlayer distance, respectively.⁴⁴ (f) Capacity of all intercalated MoS₂ 50 mA g^{-1} arranged according to conductivity, respectively.⁴⁴ (g) Schematic of intercalation of molecules into MoS₂.⁴⁴

electrospinning and high temperature carbonization. MoS₂/ CNFs have a large specific surface area and high electrical conductivity, which enhances Na storage performance.40

The MoS₂-C hollow rhomboids (MCHRs) were fabricated by a sample one-pot solvothermal reaction (Fig. 3b). First of all, manganese(II)acetylacetonate (Mn(acac)2), molybdenyl acetylacetonate (MoO₂(acac)₂) were dispersed in distilled water and isopropanol. And then, glucose and thiourea were incorporated

into the mixture. Finally, the mixture was annealed after reaction in a Teflon-lined autoclave and washed several times with dilute hydrochloric acid and deionized water to obtain MCHRs. Electrochemical measurements revealed that MCHRs had better Na storage performance, higher rate capability, more stable cycling performance and superior reversible specific capacity.41

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The vertically oxygen-incorporated MoS₂ nanosheets coated on carbon fiber (OMSCF) were synthesized by hydrothermal process and calcination reaction in air. First, carbon fiber was extracted from commercial wet tissue (Vinda Paper Group) with concentrated hydrochloric acid. Second, graphite oxide (GO) was synthesized through the modified Hummers' method. Finally, MoS₂/carbon fibers (MSCF) were obtained by hydrothermal method. The FESEM images of OMSCF are shown in Fig. 3c. Oxygen atoms are incorporated into MoS₂ by the MSCF calcined in air. The incorporation of oxygen not only creates more defects, but also expands the interlayer spacing. The composite of carbon fiber and MoS₂ nanosheets not only

improves electronic conductivity, but also enhances structural stability.⁴³

In addition, Zhang *et al.*⁴⁵ prepared ternary $MoS_{2-x}Se_x$ alloy/graphene ($MoS_{2-x}Se_x/G$) composite though hydrothermal reaction and selenization treatment (Fig. 3d). The interlayer spacing of MoS_2 is expanded due to the doping of Se atoms which facilitates Na^+ fast transfer. Meanwhile, the electronic conductivity of composite is enhanced due to graphene, which boosts the electrochemical performance for NIBs.

Dai *et al.*⁴⁴ reported a series of molecule-intercalated MoS_2 as anode materials for SIBs. The molecular intercalation method expands the interlayer spacing as well as increases the electrical

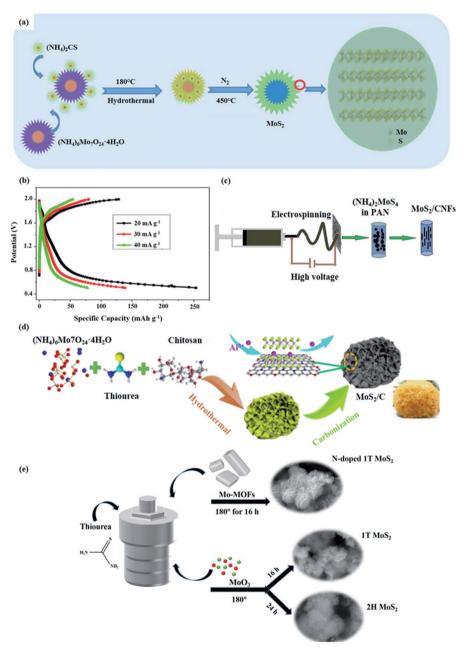


Fig. 4 (a) Schematic illustration of MoS_2 microspheres prepared by hydrothermal method.⁴⁷ (b) The first discharge-charge curves at different current densities.⁴⁷ (c) Schematic illustration of the preparation process of $MoS_2/CNFs$.⁴⁸ (d) The preparation process of MNC.⁴⁹ (e) The synthesis of N-doped 1T MoS_2 , pure 1T MoS_2 , and 2H MoS_2 .⁵⁰

conductivity of MoS₂ (Fig. 3e and f). The interlayer spacing can be varied in the range of 0.62 to 1.26 nm precisely by inserting different molecules (Fig. 3g).

In the example of the dimethylacetamide– MoS_2 (DAM– MoS_2) construct, MoS_2 was synthesized by hydrothermal method firstly. Second, squeezing small DAM molecules into the layers. ⁴⁶ Specifically, DAM, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, $Na_2S\cdot 9H_2O$, $N_2H_4\cdot H_2O$ and deionized water were mixed. Then, the mixture was placed in Teflon-liner autoclave and heated at 230 °C for 24 h. Finally, dark powders were collected after naturally cooled to RT. Benefiting from the expanded interlayer spacing and improved conductivity, the electrochemical performance of SIBs with MoS_2 as the electrode material has been enhanced.

2.3 Other rechargeable batteries

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Aluminum ion batteries (AIBs) are also members of energy storage systems. MoS_2 and its composites can be used as cathode materials for AIBs. Li *et al.*⁴⁷ prepared MoS_2 microspheres structure by hydrothermal method. The preparation process is shown in the Fig. 4a. First, the MoS_2 microsphere precursor was synthesized by using $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ and $(NH_4)_2CS$ in a hydrothermal method. And then, MoS_2 microsphere was obtained by heat treatment in a nitrogen atmosphere.

Fig. 4b depicts the electrochemical performance of MoS_2 microspheres. Obviously, the electrochemical performance of AIBs with MoS_2 microsphere cathode material is not excellent. The reason for this can be attributed to the inherent defects of MoS_2 . Therefore, future research focusing on enhancing the electrochemical properties of MoS_2 electrode materials is needed.

Yang *et al.*⁴⁸ reported a flexible free-standing MoS₂/CNFs cathode for rechargeable AIBs. As shown in Fig. 4c, the MoS₂/CNFs are prepared by electrospinning and annealing treatment. As electrode materials for AIBs, MoS₂/CNFs exhibit better cycling stability and higher rate capacity than MoS₂ microspheres.

In order to overcome the defects of MoS₂ and achieve the improved electrochemical performance of AIBs, another method is to use N-doped carbon materials compounded with MoS₂ as a cathode material for AIBs. Guo *et al.*⁴⁹ synthesized interlayer-expanded MoS₂/N-doped carbon (MNC) with a three-dimensional (3D) hierarchical structure by a hydrothermal method and calcination. Fig. 4d represents the synthesis of MNC. Electrochemical test results illustrated that MNC had excellent cycling ability and high discharge capacity, which were owing to the unique 3D structure provides a large specific surface area and the N-doped carbon expands the interlayer spacing of MoS₂.

Aqueous zinc ion batteries (ZIBs) are one of the rechargeable batteries based on divalent cations. Nevertheless, Zn^{2+} has strong interactions with water molecules, increasing the difficulty of Zn^{2+} diffusion and intercalation,⁵⁴ which hinders the development of ZIBs. To address these problems, researchers used MoS_2 as an electrode material to improve the electrochemical performance of ZIBs by increasing its interlayer spacing through doping with nitrogen or oxygen.^{50,54}

In the example of the N-doped MoS_2 , Mo-organic framework (Mo-MOF) served as the nitrogen source. Basing on the one-step hydrothermal sulfurization, N-doped MoS_2 was prepared. ⁵⁰ Ideally, the 1T and 2H phases of MoS_2 can be obtained by different reaction conditions (Fig. 4e).

The electrochemical test results illustrated that N-doped 1T MoS₂ has not only high multiplicative performance but also superior cycling stability, which greatly improves the electrochemical performance of ZIBs.

In order to better display the synthesis and application of MoS₂-based nanomaterials in electrode materials, the preparation methods and batteries performance are summarized in Table 1. In addition, we also collected some typical nanomaterials for battery applications to compare with MoS₂.⁵¹⁻⁵³

Applications and synthesis strategies of MoS₂ in catalyst for water splitting

The use of large amounts of fossil fuels has led to increasing environmental degradation, therefore, it is essential to produce clean, renewable energy. Hydrogen energy, as one of the clean energy sources, has been widely researched in recent years. Electrocatalytic water splitting and photocatalytic water splitting are recognized as efficient methods for the preparation of hydrogen. ⁵⁵⁻⁶⁰ The water splitting reaction requires an efficient catalyst. It is well known that MoS₂ is a lamellar structure with abundant active sites at the edges. This property makes it a promising non-precious metal catalyst with large numbers of applications in catalysis. However, the defects of MoS₂ with low bulk conductivity and anisotropic electrical transport restrict the catalytic efficiency. Therefore, researchers have developed amount of MoS₂ composite catalysts to improve the catalytic efficiency.

3.1 Electrocatalyst

According to previous reports, either 1T-phase MoS2 catalysts or MoS₂ composites catalysts have efficient catalytic performance in the HER. In detail, 1T-phase MoS2 has higher catalytic performance than 2H-phase MoS2, benefiting from the fast charge transfer rate in the metal phase.⁶¹ The compounding of MoS₂ with MoN can not only improve the electrical conductivity of MoS2, but also make MoS2 have good stability in acidic and alkaline environments.62 The compounding of MoS2 with CNFs can improve the electrical conductivity of MoS2 and restrict the growth of MoS₂ nanosheets. 63 In addition, MoS₂ composites can be used as bifunctional and efficient electrocatalysts for water splitting. For example, CoS₂-C@MoS₂ exhibits both excellent HER catalytic performance and good oxygen evolution reaction (OER) catalytic performance.⁶⁴ MoS₂ compounded with Mo₂Ncontaining multichannel hollow CNFs (Mo2N-MoS2 MCNFs) also possesses excellent HER and OER catalytic properties. 65 Subsequently, the preparation of these materials will be

 $1T\text{-MoS}_2$ was synthesized by hydrothermal reaction. Specifically, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and N_2H_4CS were dissolved in

Table 1 MoS₂-based nanocomposites for electrode materials

No.	Materials	Preparation	Mo source	S source	Morphology of MoS ₂	Battery electrodes	Specific capacity (mA h g^{-1})	Cycling number	Current rate $(mA g^{-1})$	Ref.
7 7	MoS ₂ MoS ₂ /C/C	Wet etching method Hydrothermal and electrospinning	$Na_2MoO_4 \cdot 2H_2O = (NH_4)_6Mo_7O_{24} \cdot 4H_2O$	Sulfur $ m N_2H_4CS$	Nanotube Sphere	LIBs cathode LIBs anode	1150 1062	250 150	200	36 34
8	${ m TiO}_2/{ m C/MoS}_2$	Solvent-thermal method and calcination	$({ m NH_4})_6{ m Mo_7O_{24}\cdot 4H_2O}$	N_2H_4CS	Fish-scale- shaped (10 nm in size)	LIBs anode	621	100	100	35
4 3	MoS ₂ /C MoS ₂ /CNFs	Template method Electrospinning and high temperature carbonization	$Na_2MoO_4 \cdot 2H_2O$ AMT	$ m N_2H_4C_S$ AMT	Nanosheet Single-layer structure	SIBs anode SIBs anode	484.9 485	1500	2000	42
9	MCHRs	One-pot solvothermal reaction	$\mathrm{MoO}_2(\mathrm{acac})_2$	N_2H_4CS	Nanosheet	SIBs anode	265	3000	10 000	41
^	OMSCF	Hydrothermal process and calcination reaction	$\mathrm{Na_2MoO_4}$	$ m N_2H_4CS$	Nanosheet	SIBs anode	330	100	100	43
&	$MoS_{2-x}Se_x/G$	Hydrothermal reaction and selenization treatment	$\left(\mathrm{NH_4}\right)_6\mathrm{Mo}_7\mathrm{O}_{24}\cdot4\mathrm{H}_2\mathrm{O}$	$ m N_2H_4CS$	ſ	SIBs anode	178	200	2000	45
6	DAM-MoS ₂	Hydrothermal method	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	$\mathrm{Na_2S \cdot 9H_2O}$	Layered structure (0.62– 1.24 nm in size)	SIBs anode	420	009	100	44
11	$ m MoS_2$ $ m MoS_2/CNFs$	Hydrothermal method Electrospinning and annealing treatment	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ $(NH_4)_2MoS_4$	N_2H_4CS $(NH_4)_2MoS_4$	Microsphere Nanosheet	AIBs cathode AIBs cathode	66.7 130	100	40	47
12	MNC	Hydrothermal method and calcination	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	$ m N_2H_4CS$	Nanosheet	AIBs cathode	127.5	1700	1000	49
13	N -doped MoS_2	One-step hydrothermal sulfurization	Mo-MOF	$ m N_2H_4CS$	Nanoflower	ZIBs cathode	98.1	1000	3000	50
14	hBN/C	Liquid-phase shear exfoliation method	I	I	I	LIBs separators	158	100	I	51
15	rGO/Al	Electrospraying	1	I	1	$\mathrm{LiNi_{0.5}Mn_{1.5}O_4}$ cathode	109.5	840	I	52
16	$\mathrm{P_4Nb_2O_{15}@CNTs}$	Solvothermal method	1	1		LIBs anode	250	200		53

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distilled water to form a homogeneous solution, and then the solution was put into a Teflon-lined stainless steel autoclave for reaction. The formation of 1T phase or 2H phase depends on the reaction temperature.

Hierarchical MoS₂/MoN heterostructures were obtained by a simple hydrothermal reaction and nitridation treatment. MoS₂ nanospheres were synthesized from N₂H₄CS and hexaammonium molybdate in a hydrothermal reaction. Subsequently, the layered MoS₂/MoN heterostructures were synthesized by nitriding under ammonia atmosphere.

MoS₂-carbon CNFs were prepared by electrospinning and graphitization treatment. First, (NH₄)₂MoS₄ was dissolved in PAN solution and used for electrospinning to prepare PAN/

(NH₄)₂MoS₄ (PANAMo) nanofibers. Afterwards, the precursor nanofibers were graphitized to obtain MoS₂-CNFs hybrids.

CoS2-C@MoS2 core-shell nanofibers were fabricated by electrospinning method, carbonization treatment and hydrothermal synthesis. First, a certain amount of PAN and Co(Ac)₂·4H₂O were dissolved in DMF to prepare Co(Ac)₂/PAN membranes by electrospinning method. Later, the Co-C nanofibers were obtained by carbonization under Ar atmosphere. Second, CoS2-C@MoS2 core-shell nanofibers were prepared by a simple hydrothermal method using (NH₄)₂MoS₄ as the S source.

As depicted in Fig. 5a, the synthesis of Mo₂N-MoS₂ MCNFs was achieved by a four-step procedure. First, a certain amount

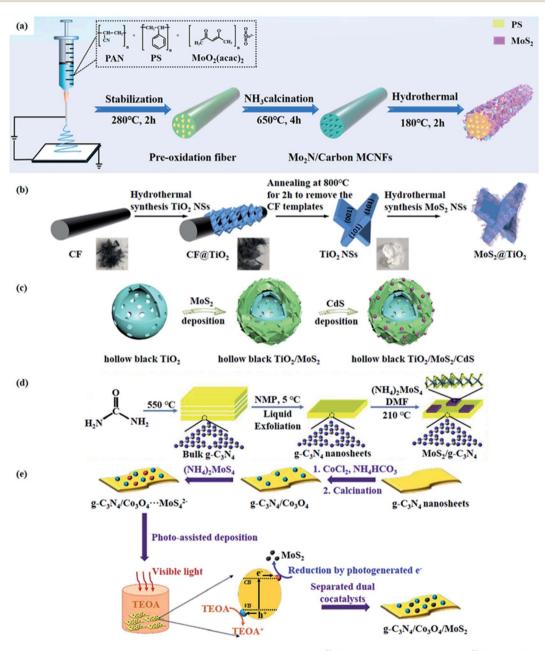


Fig. 5 The diagrammatic sketch for the preparation of (a) Mo₂N-MoS₂ MCNFs,⁶⁵ (b) MoS₂@TiO₂ composites,⁶⁸ (c) TiO₂/MoS₂/CdS tandem heterojunction, ⁶⁹ (d) 2D–2D MoS₂/g-C₃N₄ composites⁷⁰ and (e) g-C₃N₄/Co₃O₄/MoS₂ heterojunction. ⁷¹

Table 2 MoS₂-based nanocomposites for electrocatalyst and photocatalyst

						Electrocatalyst		
						a frame no no no		
No.	Materials	Preparation	Mo source	S source	Morphology of MoS_2	Tafel slope (mV dec^{-1})	Overpotential (mV ν s. RHE) at $J=10$ mA cm ⁻²	Ref.
1 2	1T-MoS_2 $ ext{MoS}_2/ ext{MoN}$	Hydrothermal reaction Hydrothermal reaction and	$(\mathrm{NH_4})_6\mathrm{Mo_7O_{24}}\cdot 4\mathrm{H_2O}$ Hexaammonium	Thiourea Thiourea	Nanosheet Nanosphere	54 (HER) 98 (HER, KOH); 87	214 (HER) 132 (HER, KOH); 117 (HER,	61 62
	ı	nitridation treatment	molybdate		•	(HER, H_2SO_4)	$H_2SO_4)$	
3	$\mathrm{MoS}_2/\mathrm{CNFs}$	Electrospinning and graphitization treatment	$(\mathrm{NH_4})_2\mathrm{MoS_4}$	$(\mathrm{NH_4})_2\mathrm{MoS_4}$	Nanoplate	42 (HER)	93 (HER)	63
4	CoS ₂ -C@MoS ₂	Electrospinning method,	$(\mathrm{NH_4})_2\mathrm{MoS_4}$	$(\mathrm{NH_4})_2\mathrm{MoS}_4$	Nanosheet	61 (HER); 46 (OER)	173 (HER); 391 (OER)	64
		hydrothermal synthesis						
S	$ m Mo_2N-MoS_2$ $ m MCNFs$	Electrospinning method, NH ₃ calcination and hydrothermal synthesis	$\mathrm{(NH_4)_6Mo_7O_{24}\cdot 4H_2O}$	Thiourea	Nanosheet	68.9 (HER); 57.2 (OER)	131 (HER); 270 (OER)	65
9	Graphene-hBN	Exfoliation and Hummer's method	I	I	I	I	390 (HER)	99
_	Cobalt- and	Annealing strategy	I	1	I	73 (OER)	210 (OER)	29
	nitrogen- codoped graphene	0						;
						Photocatalyst		
No.	Materials	Preparation	Mo source	S source	Morphology of MoS_2	H_2 evolution rate oS ₂ (mmol h ⁻¹ g ⁻¹)	Ref.	
∞	MoS ₂ @TiO ₂	Hydrothermal/annealing	$(\mathrm{NH_4})_2\mathrm{MoS_4}$	$(NH_4)_2MoS_4$	Nanosheet	2.16	89	
		treatment and subsequent photoreduction method						
6	TiO ₂ /MoS ₂ /CdS	Template-free solvothermal approach, solvothermal approach and wet chemical method	MoO_3	Thiourea	Nanosheet	6	69	
10	$\mathrm{MoS}_{2}/\mathrm{g}\text{-}\mathrm{C}_{3}\mathrm{N}_{4}$	Direct heating of urea and a solvent-thermal method	$(\mathrm{NH_4})_2\mathrm{MoS_4}$	$(\mathrm{NH_4})_2\mathrm{MoS_4}$	Nanosheet	1.155	70	
11	$\begin{array}{l} g\text{-}C_3N_4/Co_3O_4/\\ MoS_2 \end{array}$	Two-step thermal treatment, coprecipitation-calcination strategy and <i>in situ</i> photo-	$(\mathrm{NH_4})_2\mathrm{MoS_4}$	$(\mathrm{NH_4})_2\mathrm{MoS}_4$	MoS ₂ nanocrystal	5.25	71	
		deposition						
12	Sulfur-doped h- BN	CVD	I	I	I	1.3485	72	

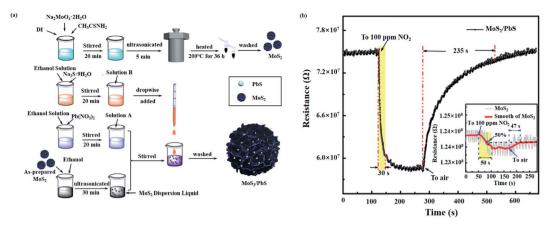


Fig. 6 (a) Preparation process of MoS₂/PbS composites.⁷⁸ (b) Transient response characteristic of MoS₂/PbS gas sensor at 100 ppm NO₂.⁷⁸

of PAN and polystyrene (PS) were dissolved in DMF, stirred well and then MoO₂(acac)₂ was added to form a precursor solution for electrospinning to obtain MoO2(acac)2@PAN/PS fiber. Second, previously obtained fiber was pre-oxidized in air. Third, Mo₂N/C MCFs were prepared by calcination of the pre-oxidation fiber under NH3 atmosphere. During calcination, PS gradually decomposed, leading to the formation of channels in the fibers. Finally, Mo₂N-MoS₂ MCNFs were successfully prepared by

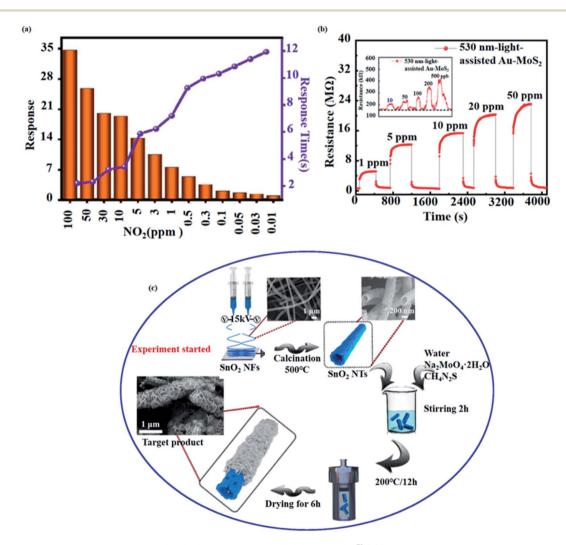


Fig. 7 (a) Response and response time of $MoS_2@SnO_2$ sensor to 0.01-100 ppm NO_2 . 79 (b) Real-time sensing response curves of the 530 nmlight-assisted Au-MoS₂ sensor at 1–50 ppm NO₂.80 (c) Schematic diagram of the synthesis of MoS₂@SnO₂.75

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hydrothermal method to grow MoS₂ nanosheets on the surface of Mo₂N/Carbon MCNFs.

3.2 Photocatalyst

Photocatalytic water splitting reaction is considered as one of the effective ways to prepare green, renewable energy, due to its ability to convert solar energy into hydrogen energy. In recent years, with the development of hydrogen preparation reaction by photocatalytic water splitting, more and more photocatalysts have been studied and prepared, including those prepared with graphite carbon nitride (g-C₃N₄), TiO₂ or CdS as materials. It has been shown that the compound of MoS₂ with the above materials can improve the catalytic activity of the photocatalyst and promote the preparation of hydrogen by water splitting. $^{68-71,73}$

Hu et al.⁶⁸ prepared MoS₂@TiO₂ composites by using combination of hydrothermal/annealing treatment with subsequent photoreduction method. It is noted that MoS₂ nanosheets can be selectively deposited on the (101) facets of TiO₂, allowing for increased photocatalytic hydrogen production activity of the MoS₂@TiO₂ composites. Sun et al.⁶⁹ fabricated a hollow TiO₂/MoS₂/CdS tandem heterojunction via three main steps. First, the hollow mesoporous TiO₂ spheres were synthesized by a template-free solvothermal approach. Second, MoS₂ nanosheets were coated on the surface of TiO₂ by a solvothermal approach. Finally, CdS nanoparticles were selectively deposited on the edges of MoS₂

nanosheets though a wet chemical method. MoS₂ not only serves as an excellent cocatalyst, but also promotes charge separation and effectively inhibits the complexation of photogenerated electrons and holes. Yuan *et al.*⁷⁰ obtained 2D–2D MoS₂/g-C₃N₄ photocatalyst though a simple probe sonication assisted liquid exfoliation method and a solventhermal method. The large surface area of g-C₃N₄ nanosheets and the large 2D nanointerface between MoS₂ and g-C₃N₄ nanosheets greatly enhance the catalytic hydrogen production activity of the photocatalyst. Zhao *et al.*⁷¹ synthesized g-C₃N₄/Co₃O₄/MoS₂ heterojunction *via* chemical deposition and photo-deposition method. Co₃O₄ and MoS₂ were used as co-catalysts with efficient photocatalytic activity under visible light irradiation. Their synthesis schematic is demonstrated in Fig. 5b–e.

In order to better display the synthesis and application of MoS_2 -based nanomaterials in catalysis, the preparation methods and catalytic performance are summarized in Table 2. Furthermore, for comparison, we summarize performance parameters of some typical nanomaterials in electrocatalysis and photocatalysis at the end of the table. 66,67,72

4. Applications and synthesis strategies of MoS₂ in gas sensors

Important factors affecting the performance of gas sensors have been reported to include specific surface area, semiconductor properties, and redox reaction active sites.⁷⁴ As mentioned

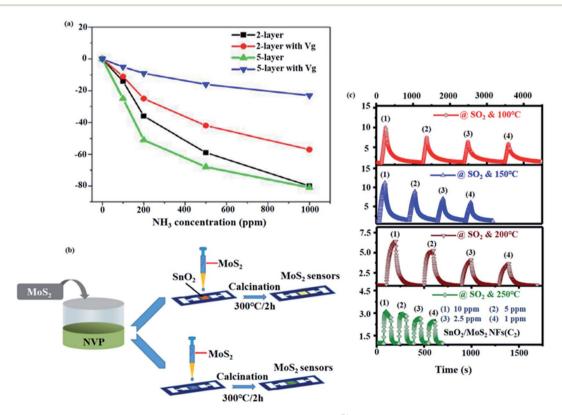


Fig. 8 (a) Sensitivity of 2-layer and 5-layer MoS_2 as a function of NH_3 concentration.⁷⁴ (b) Schematic diagram of the fabrication of MoS_2 sensors and MoS_2/SnO_2 sensors.⁸¹ (c) Response of MoS_2/SnO_2 sensors to different concentrations of SO_2 gas at different operating temperatures.⁸¹

earlier, MoS_2 is a graphene-like material possessing a 2D layer structure with a large specific surface area and excellent semi-conductor properties. In addition, it has been pointed out that MoS_2 has different affinities for different molecules,⁷⁵ which makes MoS_2 one of the promising materials for the preparation of gas sensors.

4.1 MoS₂-based gas sensors toward nitrogen dioxide

Nitrogen dioxide (NO₂) is one of the prevalent pollutants in the air, as well as a toxic gas that endangers human health, causing great damage to human eyes and respiratory tracts even when exposed to concentrations as low as 3 ppm.⁷⁶ Therefore, it is urgent to develop gas sensors that can detect NO₂ effectively and rapidly. The detection of NO₂ by pure MoS₂ or MoS₂ composites as gas-sensitive elements is one of the main focuses of gas sensors research in recent years.

Using pure MoS₂ as gas sensitive element, some researches have prepared MoS₂ by chemical vapor deposition (CVD) method. For instance, Kumar *et al.*⁷⁷ obtained 2D MoS₂ by CVD

with MoO₃ powder and sulfur as precursors. The test results revealed that the MoS2 gas sensor had a response time of 29 s and a recovery time of 350 s for 100 ppm concentration of NO₂ when operating in a RT environment irradiated by UV lamps (\sim 365 nm). Similarly, Kim et al. ¹³ fabricated layer-controlled MoS₂ by CVD with molybdenum hexacarbonyl (Mo(CO)₆) and hydrogen sulfide (H₂S). It is found that the Schottky barrier changes due to the change in the number of MoS₂ layers, which results in an improved response of the gas sensor. Zheng et al.75 synthesized n-type and p-type MoS2 films by CVD and softchemistry route, respectively. In CVD process, MoO3 and sulfur were used as precursors, while in the soft-chemistry route, molybdate sol-gel (contain 1% W) was used as precursors. Uniquely, they prepared a novel p-n junction gas sensor by stacking n-type and p-type MoS₂ atomic layers. The results represented that compared with n-type MoS₂ gas sensor, the ptype MoS₂ has a faster response to NO₂. More importantly, the p-n junction sensor not only has a 20-fold increase in sensitivity to 20 ppm NO₂, but also has a lower detection limit of 8 ppb.

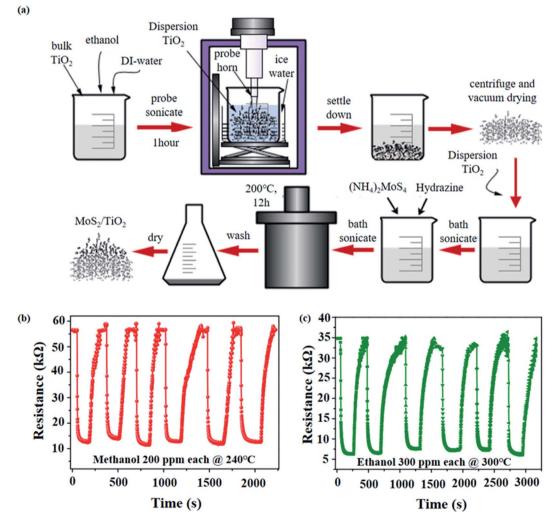


Fig. 9 (a) Schematic diagram of the synthesis of MoS_2/TiO_2 composite.⁸² (b) Repeatability testing of 200 ppm methanol for six consecutive cycles at an operating temperature of 240 °C.⁸² (c) Repeatability testing of 300 ppm methanol for six consecutive cycles at an operating temperature of 300 °C.⁸²

Table 3 MoS₂-based nanocomposites for gas sensors

No.	Materials	Preparation	Mo source	S source	Morphology	Target Gas	Res/Rec (s)	Response $(R_{\rm g}/R_{\rm a})$	$T(^{\circ}\mathrm{C})$	Detection limits	Ref.
\vdash	MoS_2	CVD	MoO_3	Sulfur	Film	100 ppm of NO_2	29/350	1.3516	RT (UV)	I	77
2	MoS_2	CVD	$Mo(CO)_6$	H_2S	Film	10 ppm of NO_2	<u> </u>	1.6	RT	1	13
3	MoS_2	CVD	MoO_3	Sulfur	Film	20 ppm of NO_2	150/30	1	RT (UV)	8 ppb	75
4	MoS_2/PbS	Hydrothermal method	$\mathrm{Na_2MoO_4 \cdot 2H_2O}$	$\mathrm{CH_3CSNH_2}$	Fluffy ball-	100 ppm of NO_2	30/235		RT	1	78
		combined with chemical			like structure						
	()	precipitation					1			•	í
2	$\mathrm{MoS}_2(\widehat{\mathrm{a}})\mathrm{SnO}_2$	Electrospinning and hydrothermal growth	$\mathrm{Na_2MoO_4 \cdot 2H_2O}$	N_2H_4CS	Nanotlake	$100 \mathrm{\ ppm}$ of NO_2	2.2/10.54	0.02884	KT.	10 ppb	6/
9	$Au-MoS_2$	Hydrothermal method	$\mathrm{Na_2MoO_4 \cdot 2H_2O}$	$\mathrm{CH_3CSNH_2}$	Fluffy flower-	1 ppm of NO_2	/27	8.1	RT	$10 \mathrm{~ppb}$	80
					like structure				(530 nm LED)		
^	MoS_2	Micromechanical exfoliation	$\operatorname{Bulk}_2\operatorname{MoS}_2$	$\operatorname{Bulk} \operatorname{MoS}_2$	Layered	$1000~\rm ppm~of~NO_2$	_/_	14.72	RT	1	74
		method	crystal	crystal							
&	MoS_2	Micromechanical exfoliation	Bulk MoS_2	$\operatorname{Bulk} \operatorname{MoS}_2$	Layered	1000 ppm of NH_3	_/_	1.86	RT	1	74
		method	crystal	crystal							
6	$\mathrm{SnO}_2/\mathrm{MoS}_2$	Electrospinning and drop- coated process	MoS ₂ powder	MoS ₂ powder	Nanosheet	$10~ m ppm~of~SO_2$	_/_	11.1	150	5 ppt (parts- per-trillion)	81
10	$\mathrm{MoS}_2/\mathrm{TiO}_2$	Low-cost hydrothermal	$(\mathrm{NH_4})_2\mathrm{MoS_4}$	$(\mathrm{NH_4})_2\mathrm{MoS}_4$	Layered	500 ppm of	50/100	nearly 0	300	. 1	82
7		ineurod.	0-94 (1114)	0-34 (1114)		culanoi 700 f		į			ć
11	$1002/110_2$	nethod	$(1$ N 1 4 $)$ 2 1 MOS $_4$	(1N 1 4 $)$ 2 1 M 0 3 4	гауетеп	aco ppin or methanol	 -	CT.0	740	I	70
12	CuO/rGO	LbL self-assemble	1	1	1	1 ppm of CO	70/160	1.0256	RT	1	83
13	Single-walled		1	I	l	100 ppb of NO	_/_	0.7136	RT		84
	carbon										
	nanotubes										
14	Graphene oxide	Thermal reduction	1	1	1	5 ppm of NO_2	_/_	0.83	RT	1	82
15	DETA doped	CVD and vapor-phase	1	1	1	50 ppm of NO_2	_/_	0.23	RT	0.83 ppq	98
	graphene	molecular doping								(parts per quadrillion)	

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Just as pure MoS2 gas sensors exhibit gas-sensitive performance on NO2 gas, MoS2 composite gas sensors also have excellent gas-sensitive properties. For example, the PbS quantum dots modified MoS2 (MoS2/PbS) composite gas sensor prepared by Xin et al. 78 has excellent gas-sensitive performance for NO₂ due to the high response of PbS quantum dots to NO₂ and the prevention of MoS₂ oxidation. MoS₂/PbS was prepared by hydrothermal and chemical precipitation methods, and the specific preparation is shown in Fig. 6a. First of all, pure MoS₂ was prepared from Na2MoO4·2H2O and CH3CSNH2 by hydrothermal reaction under an Teflon-lined autoclave at 200 °C. Secondly, the doping of PbS quantum dots was achieved by chemical precipitation using Na₂S·9H₂O and Pb(NO₃)₂ as precursors. Compared with pure MoS2, the MoS2/PbS gas sensor has higher response and recovery performance for 100 ppm NO₂ gas at RT (Fig. 6b).

Composites of MoS₂ nanosheets with SnO₂ nanotubes were prepared for gas-sensitive properties by Bai *et al.* MoS₂@SnO₂ heterostructure exhibits impressive sensitivity and selectivity for the detection of NO₂ gas at RT. Tests illustrated that the MoS₂@SnO₂ gas sensor had a fast response time (2.2 s), a short recovery time (10.54 s), a low detection limit (10 ppb) and excellent stability (20 weeks) (Fig. 7a).⁷⁹ Another reported composite is MoS₂ nanoflowers modified with Au nanoparticles prepared by Chen *et al.* Surprisingly, the Au–MoS₂ gas sensor exhibits an extremely low detection limit (10 ppb) for NO₂ at RT with strong resistance to moisture interference under 530 nm light illumination (Fig. 7b).⁸⁰

The preparation of MoS₂@SnO₂ was achieved by electrostatic spinning and hydrothermal methods, as presented in Fig. 7c. First, stannous chloride (SnCl₂·2H₂O) was mixed with anhydrous ethanol, DMF and PVP to make electrospinning solution, and SnO₂ NTs were obtained by spinning technique and subsequent high-temperature calcination treatment. Second, N₂H₄CS and Na₂MoO₄·2H₂O were used as the S and Mo sources, respectively, to mix with the previously prepared SnO₂ NTs, and the reaction was carried out in an autoclave at 200 °C to realize MoS₂ on SnO₂ NTs growth.⁷⁹

The fabrication of Au–MoS $_2$ composites was achieved by a two-step hydrothermal method. Firstly, MoS $_2$ was obtained by reacting Na $_2$ MoO $_4\cdot 2H_2$ O and thioacetamide (CH $_3$ CSNH $_2$) in a Teflon-lined autoclave at 200 °C for 36 h. Secondly, Au–MoS $_2$ was synthesized by mixing sodium citrate tribasic dihydrate (C $_6$ H $_5$ Na $_3$ O $_7\cdot 2$ H $_2$ O), tannic acid (C $_7$ 6H $_5$ 2O $_4$ 6) and previously prepared MoS $_2$, then adding gold chloride trihydrate (HAuCl $_4$ ·3H $_2$ O) solution dropwise and stirring well, and then reacting in a Teflon-lined autoclave.

4.2 MoS₂-based gas sensors for other gases

The MoS_2 -based gas sensors not only detect NO_2 gas extremely well, but also reveal excellent gas sensitivity to NH_3 , SO_2 and alcohol gases.

Dattatray J. Late et~al.⁷⁴ prepared layered MoS $_2$ films by micromechanical exfoliation method in 2013 for the preparation of gas sensors to detect NH $_3$ gas. The experimental results demonstrated that the 2-layer MoS $_2$ and 5-layer MoS $_2$ have

excellent gas-sensitive performance to NH₃, and the 5-layer MoS₂ is more sensitive to detect NH₃. In addition, when the MoS₂ gas sensor is applied with a positive gate voltage, the electric field formed at the interface will repel the electrons given by NH₃ as an electron donor, resulting in a decrease in the sensitivity of MoS₂ to NH₃. Fig. 8a shows the curves of sensitivity with NH₃ concentration for 2-layer and 5-layer MoS₂ with and without gate voltage.

Nguyen Ngoc Viet *et al.*⁸¹ prepared MoS₂/SnO₂ sensors for SO₂ gas detection by on-chip electrostatic spinning and subsequently dropping MoS₂ nanosheets-dispersed solution, and the fabrication is depicted in Fig. 8b. The test results indicated that the MoS₂/SnO₂ gas sensor had good gas-sensitive performance for 10 ppm SO₂ gas at 150 °C (Fig. 8c).

Sukhwinder Singh *et al.*⁸² prepared MoS_2/TiO_2 composite for the detection of methanol and ethanol. As shown in Fig. 9a, MoS_2/TiO_2 hybrid was obtained by two steps: first, pure TiO_2 powder was mixed with ethanol and other solvents for probe sonication, and second, $(NH_4)_2MoS_4$ was mixed with the produced TiO_2 suspension to prepare MoS_2/TiO_2 composites by hydrothermal method. The test results revealed that the best working temperatures of MoS_2/TiO_2 composites for methanol and ethanol were 240 °C and 300 °C, respectively, and more importantly, the MoS_2/TiO_2 sensor had good response and better stability (Fig. 9b and c).

The gas sensing performance of MoS₂-based nanomaterials and the preparation methods are listed in Table 3. As a comparison, the gas-sensitive properties of some typical materials are collected at the end of the table.⁸³⁻⁸⁶

5. Conclusion

This review highlights recent advances in MoS₂-based materials synthesis and their applications toward batteries, catalysts and gas sensors. First of all, MoS2, due to the large specific surface area and abundant active sites, has become one of the most popular electrode materials. In addition, the compound of MoS₂ with CNFs and TiO₂ materials overcomes the inherent defects of MoS2 and greatly improves the electrochemical performance of the battery. Second, MoS₂ has catalytic active sites on the edges, which makes it one of the most popular candidates to replace noble metal catalysts. The composite of MoS₂ with MoN, CoS₂ and C₃N₄ improved the catalytic performance of the catalyst. Finally, MoS₂ can be used in gas sensors due to the semiconductor properties and non-zero forbidden bandwidth. The compound of MoS2 with materials such as SnO2 and PbS can enhance the sensitivity of the gas sensor to the gas to be detected and reduce the detection limit.

It is worth noting that while MoS₂ has made good progress in these areas, challenges remain in its future development. First, MoS₂ has low electrical conductivity and multilayer MoS₂ tends to accumulate and aggregate in the preparation, which is not conducive to electron transport. Second, the active sites of MoS₂ are mainly at the edges but not at the basal plane, which has a significant impact on both the sensing performance and catalytic performance. Therefore, it is necessary to further explore the compounding of MoS₂ with other materials or to

optimize the structure of MoS_2 (e.g., preparation of MoS_2 NTs, etc.). In addition, 1T- MoS_2 has better electrical conductivity compared with 2H- MoS_2 , and there are also interesting electrical properties using 1T- MoS_2 compounded with other materials

In a word, MoS_2 has promising applications in energy and gas sensors due to its excellent and unique physicochemical properties. We believe that with the joint efforts of researchers in the future, better progress will be made in the applications and synthesis of MoS_2 .

Conflicts of interest

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There are no conflicts to declare.

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References

- 1 K. S. Novoselov, D. Jiang, F. Schedin, T. Booth, V. Khotkevich, S. Morozov and A. K. Geim, *Proc. Natl. Acad. Sci.*, 2005, **102**, 10451–10453.
- 2 S. Z. Butler, S. M. Hollen, L. Cao, Y. Cui, J. A. Gupta, H. R. Gutiérrez, T. F. Heinz, S. S. Hong, J. Huang and A. F. Ismach, *ACS Nano*, 2013, 7, 2898–2926.
- 3 G. R. Bhimanapati, Z. Lin, V. Meunier, Y. Jung, J. Cha, S. Das, D. Xiao, Y. Son, M. S. Strano and V. R. Cooper, *ACS Nano*, 2015, 9, 11509–11539.
- 4 Z. Wang and B. Mi, Environ. Sci. Technol., 2017, 51, 8229-8244.
- 5 H. Wang, C. Li, P. Fang, Z. Zhang and J. Z. Zhang, *Chem. Soc. Rev.*, 2018, 47, 6101–6127.
- 6 U. Krishnan, M. Kaur, K. Singh, M. Kumar and A. Kumar, Superlattices Microstruct., 2019, 128, 274–297.
- 7 T. Nawz, A. Safdar, M. Hussain, D. Sung Lee and M. Siyar, *Crystals*, 2020, 10.
- 8 D. Saha and P. Kruse, J. Electrochem. Soc., 2020, 167.
- 9 O. Samy and A. El Moutaouakil, Energies, 2021, 14.
- 10 Y. Zhang, H. Tao, S. Du and X. Yang, ACS Appl. Mater. Interfaces, 2019, 11, 11327–11337.
- 11 R. Bose, Z. Jin, S. Shin, S. Kim, S. Lee and Y. S. Min, *Langmuir*, 2017, 33, 5628–5635.
- 12 Y. Wang, J. Sunarso, F. Wang, B. Zhao, X. Liu and G. Chen, *Ceram. Int.*, 2017, 43, 11028–11033.
- 13 Y. Kim, S. K. Kang, N. C. Oh, H. D. Lee, S. M. Lee, J. Park and H. Kim, *ACS Appl. Mater. Interfaces*, 2019, 11, 38902–38909.
- 14 Z. Liu, L. Zhao, Y. Liu, Z. Gao, S. Yuan, X. Li, N. Li and S. Miao, *Appl. Catal.*, *B*, 2019, 246, 296–302.
- 15 E. Singh, K. S. Kim, G. Y. Yeom and H. S. Nalwa, *ACS Appl. Mater. Interfaces*, 2017, **9**, 3223–3245.

- 16 X. Li and H. Zhu, J. Materiomics, 2015, 1, 33-44.
- 17 Y. Qiao, T. Hirtz, F. Wu, G. Deng, X. Li, Y. Zhi, H. Tian, Y. Yang and T.-L. Ren, ACS Appl. Electron. Mater., 2019, 2, 346–370.
- 18 Y. Liu and F. Gu, Nanoscale Adv., 2021, 3, 2117-2138.
- 19 O. Samy, S. Zeng, M. D. Birowosuto and A. El Moutaouakil, *Crystals*, 2021, 11.
- 20 Y. P. Venkata Subbaiah, K. J. Saji and A. Tiwari, *Adv. Funct. Mater.*, 2016, **26**, 2046–2069.
- 21 W. Zhang, P. Zhang, Z. Su and G. Wei, *Nanoscale*, 2015, 7, 18364–18378.
- 22 H. S. Nalwa, RSC Adv., 2020, 10, 30529-30602.
- 23 S. Barua, H. S. Dutta, S. Gogoi, R. Devi and R. Khan, *ACS Appl. Nano Mater.*, 2017, 1, 2–25.
- 24 S. Shi, Z. Sun and Y. H. Hu, J. Mater. Chem. A, 2018, 6, 23932–23977.
- 25 L. Lei, D. Huang, G. Zeng, M. Cheng, D. Jiang, C. Zhou, S. Chen and W. Wang, *Coord. Chem. Rev.*, 2019, 399, 213020.
- 26 Y. Jiao, A. M. Hafez, D. Cao, A. Mukhopadhyay, Y. Ma and H. Zhu, *Small*, 2018, **14**, e1800640.
- 27 J. Sun, X. Li, W. Guo, M. Zhao, X. Fan, Y. Dong, C. Xu, J. Deng and Y. Fu, *Crystals*, 2017, 7(7), 198.
- 28 Z. Liu, X. Wang, Z. Liu, S. Zhang, Z. Lv, Y. Cui, L. Du, K. Li, G. Zhang, M. C. Lin and H. Du, ACS Appl. Mater. Interfaces, 2021, 13, 28164–28170.
- 29 N. Qiu, Z. Yang, R. Xue, Y. Wang, Y. Zhu and W. Liu, *Nano Lett.*, 2021, **21**, 2738–2744.
- 30 S. G. Stolyarova, A. A. Kotsun, Y. V. Shubin, V. O. Koroteev, P. E. Plyusnin, Y. L. Mikhlin, M. S. Mel'gunov, A. V. Okotrub and L. G. Bulusheva, ACS Appl. Energy Mater., 2020, 3, 10802–10813.
- 31 Z. Yuan, L. Wang, D. Li, J. Cao and W. Han, *ACS Nano*, 2021, **15**, 7439–7450.
- 32 C. Zhu, X. Mu, P. A. van Aken, Y. Yu and J. Maier, *Angew. Chem.*, *Int. Ed. Engl.*, 2014, 53, 2152–2156.
- 33 C.-Y. Wei, P.-C. Lee, C.-W. Tsao, L.-H. Lee, D.-Y. Wang and C.-Y. Wen, *ACS Appl. Energy Mater.*, 2020, 3, 7066–7072.
- 34 H. Wu, C. Hou, G. Shen, T. Liu, Y. Shao, R. Xiao and H. Wang, *Nano Res.*, 2018, **11**, 5866–5878.
- 35 J. Zhang, Y. Li, T. Gao, X. Sun, P. Cao and G. Zhou, *Ceram. Int.*, 2018, 44, 8550–8555.
- 36 X. Zhao, Z. Liu, W. Xiao, H. Huang, L. Zhang, Y. Cheng and J. Zhang, *ACS Appl. Nano Mater.*, 2020, 3, 7580–7586.
- 37 S. Ding, D. Zhang, J. S. Chen and X. W. Lou, *Nanoscale*, 2012, 4, 95–98.
- 38 Y. Lu, X. Yao, J. Yin, G. Peng, P. Cui and X. Xu, *RSC Adv.*, 2015, 5, 7938–7943.
- 39 K. Yao, Z. Xu, J. Huang, M. Ma, L. Fu, X. Shen, J. Li and M. Fu, Small, 2019, 15, e1805405.
- 40 A. Cheng, H. Zhang, W. Zhong, Z. Li, Y. Tang and Z. Li, *J. Electroanal. Chem.*, 2019, **843**, 31–36.
- 41 L. Han, S. Wu, Z. Hu, M. Chen, J. Ding, S. Wang, Y. Zhang, D. Guo, L. Zhang, S. Cao and S. Chou, ACS Appl. Mater. Interfaces, 2020, 12, 10402–10409.
- 42 Q. Pan, Q. Zhang, F. Zheng, Y. Liu, Y. Li, X. Ou, X. Xiong,C. Yang and M. Liu, ACS Nano, 2018, 12, 12578–12586.

Review

43 Y. Zhang, H. Tao, T. Li, S. Du, J. Li, Y. Zhang and X. Yang, *ACS Appl. Mater. Interfaces*, 2018, **10**, 35206–35215.

- 44 H. Dai, M. Tang, J. Huang and Z. Wang, ACS Appl. Mater. Interfaces, 2021, 13, 10870–10877.
- 45 Y. Zhang, H. Tao, S. Du and X. Yang, ACS Appl. Mater. Interfaces, 2019, 11, 11327–11337.
- 46 H. Dai, J. Sun, Y. Zhou, Z. Zhou, W. Luo, G. Wei and H. Deng, ACS Sustainable Chem. Eng., 2020, 8, 8102–8110.
- 47 Z. Li, B. Niu, J. Liu, J. Li and F. Kang, ACS Appl. Mater. Interfaces, 2018, 10, 9451-9459.
- 48 W. Yang, H. Lu, Y. Cao, B. Xu, Y. Deng and W. Cai, *ACS Sustainable Chem. Eng.*, 2019, 7, 4861–4867.
- 49 S. Guo, H. Yang, M. Liu, X. Feng, H. Xu, Y. Bai and C. Wu, *ACS Appl. Energy Mater.*, 2021, 4, 7064–7072.
- 50 Z. Sheng, P. Qi, Y. Lu, G. Liu, M. Chen, X. Gan, Y. Qin, K. Hao and Y. Tang, ACS Appl. Mater. Interfaces, 2021, 13, 34495– 34506.
- 51 A. C. M. de Moraes, W. J. Hyun, N. S. Luu, J. M. Lim, K. Y. Park and M. C. Hersam, ACS Appl. Mater. Interfaces, 2020, 12, 8107–8114.
- 52 G. Zhang, K. Lin, X. Qin, L. Zhang, T. Li, F. Lv, Y. Xia, W. Han, F. Kang and B. Li, ACS Appl. Mater. Interfaces, 2020, 12, 37034–37046.
- 53 P. Hei, S. Luo, K. Wei, J. Zhou, Y. Zhao and F. Gao, *ACS Sustainable Chem. Eng.*, 2020, **9**, 216–223.
- 54 H. Liang, Z. Cao, F. Ming, W. Zhang, D. H. Anjum, Y. Cui, L. Cavallo and H. N. Alshareef, *Nano Lett.*, 2019, **19**, 3199–3206.
- 55 L. Jia, B. Liu, Y. Zhao, W. Chen, D. Mou, J. Fu, Y. Wang, W. Xin and L. Zhao, J. Mater. Sci., 2020, 55, 16197–16210.
- 56 D. Wang, X. Zhang, S. Bao, Z. Zhang, H. Fei and Z. Wu, *J. Mater. Chem. A*, 2017, 5, 2681–2688.
- 57 X. Han, X. Tong, X. Liu, A. Chen, X. Wen, N. Yang and X.-Y. Guo, *ACS Catal.*, 2018, **8**, 1828–1836.
- 58 Y.-J. Yuan, P. Wang, Z. Li, Y. Wu, W. Bai, Y. Su, J. Guan, S. Wu, J. Zhong, Z.-T. Yu and Z. Zou, *Appl. Catal.*, *B*, 2019, 242, 1–8.
- 59 X.-L. Yin, G.-Y. He, B. Sun, W.-J. Jiang, D.-J. Xue, A.-D. Xia, L.-J. Wan and J.-S. Hu, *Nano Energy*, 2016, 28, 319–329.
- 60 Q. Li, W. Liu, L. Xiao, X. Chen and X. Xu, *Mater. Lett.*, 2021, 285
- 61 J. Wang, W. Fang, Y. Hu, Y. Zhang, J. Dang, Y. Wu, H. Zhao and Z. Li, *Catal. Sci. Technol.*, 2020, **10**, 154–163.
- 62 A. Wu, Y. Gu, Y. Xie, H. Yan, Y. Jiao, D. Wang and C. Tian, *J. Alloys Compd.*, 2021, 867.
- 63 H. Zhu, F. Lyu, M. Du, M. Zhang, Q. Wang, J. Yao and B. Guo, *ACS Appl. Mater. Interfaces*, 2014, **6**, 22126–22137.
- 64 Y. Zhu, L. Song, N. Song, M. Li, C. Wang and X. Lu, *ACS Sustainable Chem. Eng.*, 2019, 7, 2899–2905.

- 65 D. Xie, G. Yang, D. Yu, Y. Hao, S. Han, Y. Cheng, F. Hu, L. Li, H. Wei, C. Ji and S. Peng, ACS Sustainable Chem. Eng., 2020, 8, 14179–14189.
- 66 S. Bawari, N. M. Kaley, S. Pal, T. V. Vineesh, S. Ghosh, J. Mondal and T. N. Narayanan, *Phys. Chem. Chem. Phys.*, 2018, 20, 15007–15014.
- 67 Q. Zhang, Z. Duan, M. Li and J. Guan, *Chem. Commun.*, 2020, **56**, 794–797.
- 68 X. Hu, S. Lu, J. Tian, N. Wei, X. Song, X. Wang and H. Cui, *Appl. Catal., B*, 2019, **241**, 329–337.
- 69 B. Sun, W. Zhou, H. Li, L. Ren, P. Qiao, W. Li and H. Fu, *Adv. Mater.*, 2018, **30**, e1804282.
- 70 Y.-J. Yuan, Z. Shen, S. Wu, Y. Su, L. Pei, Z. Ji, M. Ding, W. Bai, Y. Chen, Z.-T. Yu and Z. Zou, Appl. Catal., B, 2019, 246, 120–128
- 71 H. Zhao, Z. Jiang, K. Xiao, H. Sun, H. S. Chan, T. H. Tsang, S. Yang and P. K. Wong, *Appl. Catal.*, B, 2021, 280.
- 72 G. Zhao, A. Wang, W. He, Y. Xing and X. Xu, *Adv. Mater. Interfaces*, 2019, **6**, 1900062.
- 73 N. Qin, J. Xiong, R. Liang, Y. Liu, S. Zhang, Y. Li, Z. Li and L. Wu, *Appl. Catal.*, *B*, 2017, **202**, 374–380.
- 74 D. J. Late, Y. K. Huang, B. Liu, J. Acharya, S. N. Shirodkar, J. Luo, A. Yan, D. Charles, U. V. Waghmare and V. P. Dravid, ACS Nano, 2013, 7, 4879–4891.
- 75 W. Zheng, Y. Xu, L. Zheng, C. Yang, N. Pinna, X. Liu and J. Zhang, Adv. Funct. Mater., 2020, 30, 2000435.
- 76 T. Pham, G. Li, E. Bekyarova, M. E. Itkis and A. Mulchandani, *ACS Nano*, 2019, **13**, 3196–3205.
- 77 R. Kumar, N. Goel and M. Kumar, *ACS Sens.*, 2017, **2**, 1744–1752.
- 78 X. Xin, Y. Zhang, X. Guan, J. Cao, W. Li, X. Long and X. Tan, *ACS Appl. Mater. Interfaces*, 2019, **11**, 9438–9447.
- 79 X. Bai, H. Lv, Z. Liu, J. Chen, J. Wang, B. Sun, Y. Zhang, R. Wang and K. Shi, *J. Hazard. Mater.*, 2021, 416, 125830.
- 80 P. Chen, J. Hu, M. Yin, W. Bai, X. Chen and Y. Zhang, *ACS Appl. Nano Mater.*, 2021, **4**, 5981–5991.
- 81 N. N. Viet, L. V. Thong, T. K. Dang, P. H. Phuoc, N. H. Chien, C. M. Hung, N. D. Hoa, N. Van Duy, N. Van Toan, N. T. Son and N. Van Hieu, *Anal. Chim. Acta*, 2021, **1167**, 338576.
- 82 S. Singh and S. Sharma, Sens. Actuators, B, 2022, 350.
- 83 D. Zhang, C. Jiang, J. Liu and Y. Cao, *Sens. Actuators*, *B*, 2017, 247, 875–882.
- 84 D.-W. Jeong, K. H. Kim, B. S. Kim and Y. T. Byun, *Appl. Surf. Sci.*, 2021, 550.
- 85 Y. R. Choi, Y.-G. Yoon, K. S. Choi, J. H. Kang, Y.-S. Shim, Y. H. Kim, H. J. Chang, J.-H. Lee, C. R. Park, S. Y. Kim and H. W. Jang, *Carbon*, 2015, 91, 178–187.
- 86 B. Kwon, H. Bae, H. Lee, S. Kim, J. Hwang, H. Lim, J. H. Lee, K. Cho, J. Ye, S. Lee and W. H. Lee, *ACS Nano*, 2022, **16**, 2176–2187.