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Morphological Characteristics of Molybdenum Disulfide and Current Application on Detecting SF_6 Decomposing Products

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MoS_2 has been considered a potential novel material in various fields due to its large specific surface area, high carrier mobility, and tunable electronic properties. However, with the increasing demand for sensor substrates, different strategies have been made to achieve its high performance, usually by adopting the method of controlling the microstructure. SF_6 gas-insulated electrical equipment has gained considerable attention in electric systems with the advantages of small volume, high security, strong breaking performance, and high-pressure fracture tolerance. Nevertheless, in the process of equipment operation, the SF_6 gas will occur inevitably decompose due to partial discharge, resulting in the deterioration of the insulation performance of the equipment. Therefore, detecting SF_6 decomposition products is significant for the safe and stable operation of power systems. In this mini review, we start from the synthesis of various MoS_2 morphological structures. Then, the beneficial characteristics of the unique synthesized nanostructures at present are analyzed. Besides, we focus on the gas-sensing mechanisms and applications of MoS_2-based sensors for detecting SF_6 decomposition products. Finally, the future development in this field is proposed.

Keywords: molybdenum disulfide, morphological characteristics, SF_6 decomposing products, sensing application, gas insulated switchgear

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INTRODUCTION

Sulfur hexafluoride (SF_6) is a non-color, tasteless, and non-flammable insulating gas, which is widely known for applications in gas insulated switchgear (GIS) (Lu et al., 2018; Lu et al., 2019). Although GIS has advantage of high stability, insulation faults such as partial discharge, breakdown discharge, and spark discharge inevitably occur during a long running process (Zeng et al., 2015; Liu et al., 2017), which will lead to the decomposition of the SF_6 gas into various sulfur fluorides, including H_2S, SO_2, SO_2F_2, and SOF_2 etc. (Wei et al., 2020). Previous research has indicated that these characteristic gases can accelerate the corrosion rate of facilities and increase the probability of system paralysis (Zhang X. X. et al., 2017a; Zhou et al., 2018b). Therefore, it is of great necessity to evaluate the operational status of GIS equipment by effectively detecting these typically decomposed products of SF_6 (Zhang X. X. et al., 2017b; Zhou et al., 2018d). In this respect, bidimensional nanomaterials have captured widespread attention for its multiple physical and chemical properties in the detection of SF_6 decomposed gas (Zhou et al., 2018a; Chen et al., 2018).

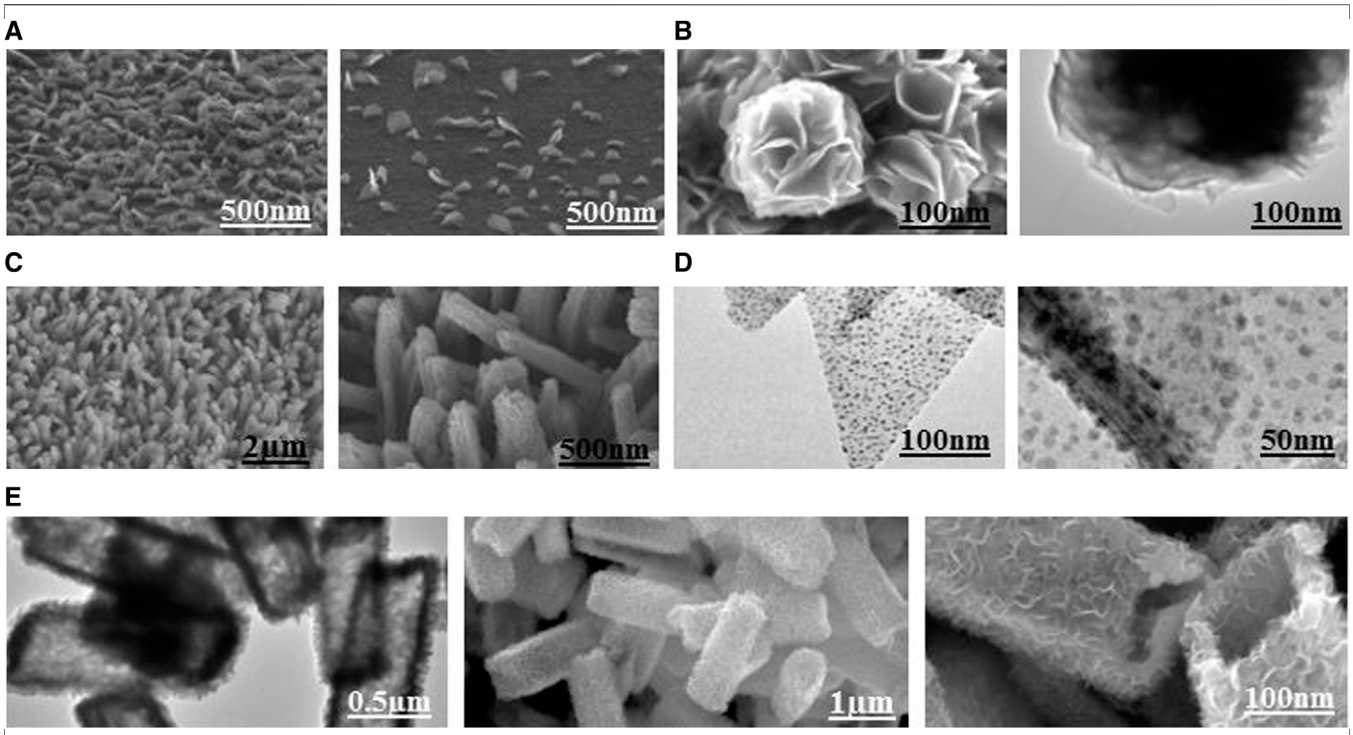

FIGURE 1 | MoS_2 with different hierarchical structures: **(A)** Vertical nanoflakes. Reprinted with permission from Kang et al. (2017). Copyright (2017) American Chemical Society. **(B)** Flower-like spheres. Reprinted with permission from Tu et al. (2019). Copyright (2019) American Chemical Society. **(C)** Nanorods. Reprinted with permission from Sun et al. (2018). Copyright (2018) American Chemical Society. **(D)** Porous film. Reprinted with permission from Li et al. (2019). Copyright (2019) American Chemical Society. **(E)** Porous hollow rhomboids. Reprinted with permission from Han et al. (2020). Copyright (2020) American Chemical Society.

Given this, various 2-D nanomaterials such as carbon nanotube (CNT), graphene, and molybdenum disulfide (MoS_2) have been synthesized by different methods (Zhou et al., 2018e; Choi et al., 2020). As an n-type semiconductor material with wide band gap, MoS_2 receives the most interest because of its high surface activity and chemical stability (Fan et al., 2017; Zhang et al., 2019). Up to now, a large number of studies have been carried out on the various nanostructures of MoS_2, including nanoflakes (Johari et al., 2020), nanotubes (Zhong et al., 2020), nanospheres (Li Y. X. et al., 2019) and other complex hierarchical nanostructures (Zhang et al., 2018b; Agrawal et al., 2020), to realize more effective methods of detecting SF_6 decomposed products. Besides, the evident correlation has been confirmed between unique structures and performances (Barzegar et al., 2019; Wang et al., 2020). Therefore, the morphology synthesis and analysis of MoS_2 nanostructures are of great significant to discuss. This mini review summarizes the morphological features and sensing applications of MoS_2, especially for detecting SF_6 decomposed products.

Morphology and analysis of MoS_2

MoS_2 is deemed as a viable and effective material owing to its stable semiconducting property and high thermal stability (Sahoo et al., 2016; Sangeetha and Madhan, 2020). Until now, the diverse morphology of MoS_2 nanostructures have been designed by investigators through various methods to achieve excellent sensing properties in the aspects of chemical, optical, and gas sensors (Zhang et al., 2018a; Bhakhar et al., 2019). Kang et al. demonstrated vertical MoS_2 nanoflakes (shown in **Figure 1A**) fabricated on SiO_2/Si substrates by the deposition and thermal evaporation. They found the vertical flakes supplied an effective surface area and sufficient oxygen vacancies for the adsorption of NO_2 gas. The minimum concentration of the NO_2 detection was 0.15 ppm at room temperature (Kang et al., 2017). Tu et al. synthesized hierarchical MoS_2 spheres with flower-like structures (shown in **Figure 1B**) presented efficient aluminum storage properties. These flower-like microstructures for aluminum storage possessed open and well-defined hierarchical structures, leading to a higher specific capacity and prominent cycling stability. The as-prepared MoS_2 electrodes delivered reversible capacities of 112.2 mAh g^{-1} at 153.6 mAh g^{-1} after 100 cycles (Tu et al., 2019).

Sun et al. developed MoS_2 nanorods (shown in **Figure 1C**) by the hydrothermal and ammonia annealing approach and found that the fabricated nanorods exhibited excellent catalytic performances due to a more specific surface area and a sufficient ion transportation channel (Sun et al., 2018). Li et al. fabricated a three-dimensional porous MoS_2 film of surface-grown Pt nanocrystals (shown in **Figure 1D**) via the CVD-TA method, and found that higher Pt loading yields improved the performances of the hydrogen evolution reaction with a smaller specific surface area. Besides, these special porous constructions could effectively solve the stacking and agglomeration problems owing to the electrochemical reaction,

guarding remarkable cycling stability (Li et al., 2019). Han et al. reported electrode material performance of hierarchically porous MoS_2-Carbon hollow rhomboids (shown in **Figure 1E**) prepared by a self-templated solvothermal reaction. The as-prepared electrodes delivered reversible capacities of 506 mAh g^{-1} at 0.1 A g^{-1} after 3,000 cycles. The authors ascribed the excellent storage energy properties of MoS_2-C rhomboids structures to the distinct internal void structure (Han et al., 2020).

MoS_2 SENSOR FOR SF_6 DECOMPOSING PRODUCTS

Theoretical calculations about MoS_2-based sensors

In order to analyze and investigate the adsorption process between SF_6 decomposed gases and MoS_2-based material, corresponding adsorbing factors containing total adsorption energies (E_{ads}), the value of charge transfer (Q_t), and projected or total density of state can be attained (Azofra et al., 2017). The calculation formula is as follows:

$$E_{ads} = E_{MoS_2/gas\ molecule} - E_{MoS_2} - E_{gas\ molecule} \quad (1)$$

$E_{MoS_2/gas\ molecule}$ is the systemic energy after reaction, $E_{gas\ molecule}$ and E_{MoS_2}, signify the energy of gas molecule and the full energies of the MoS_2 before the reaction, respectively (Wang et al., 2019c). The negative value of E_{ad} illustrates the exothermic procedure of gas adsorption and the spontaneity of reaction. Moreover, the charge transfer Q_t before and after the gas molecule adsorbed on the MoS_2 system is defined by **Eq. 2**:

$$Q_t = Q_a - Q_b \quad (2)$$

where Q_a and Q_b present the number of charge after adsorption carried by the gas and the net carried charge of isolated gas molecules, respectively (Zhao et al., 2016; Wang et al., 2019b). The negative value of Q_t presents the electrons transfer from the MoS_2-based system to gas molecules.

The adsorption procedures between gas sensing materials and SF_6 decomposing products were studied based on the density functional theory (DFT) (Singh et al., 2018; Cui et al., 2019). For instance, Abbasi et al. studied the adsorptions properties of SO_2 molecules on MoS_2 monolayers in the aspects of charge transfer, band structures, adsorption energy, and charge density differences. They found that SO_2 gas molecules were adsorbed on the surface monolayer by physisorption. The S-O bonds of the adsorption gas molecules were lengthened after the adsorbed process. Furthermore, elongation of the bond lengths was mainly owed to the transfer of charge density from the original to the new bonds between the MoS_2 monolayers and target gas molecules, and the adsorption of SO_2 changed the electronic properties of MoS_2 monolayer (Abbasi and Sardroodi 2019). Chen et al. theoretically discussed the adsorption behavior of five types of SF_6 decomposing products (H_2S, HF, SO_2, SOF_2, and SO_2F_2) on the MoS_2 monolayer by employing the NEGF combined with DFT method. Among the five types of gas molecules, MoS_2 monolayer had the best adsorption performance for SO_2 caused by the special electronegativity (Chen et al., 2019a).

TABLE 1 | Comparison of adsorption parameters for H_2S and SO_2 in different systems.

SF_6 Decomposing products	System	E_{ad} (eV)	Q_t (e)	References
H_2S	MoS_2	−0.22	0.02	Chen et al., 2019a
	Si-MoS_2	−0.68	0.16	Gui et al., 2019
	Ni-MoS_2	−1.319	0.254	Wei et al., 2018
	Pt-MoS_2	−1.465	0.302	Qian et al., 2019
SO_2	MoS_2	−0.30	−0.04	Chen et al., 2019a
	Ni-MoS_2	−1.382	−0.016	Wei et al., 2018
	Pt-MoS_2	−1.584	0.036	Qian et al., 2019
	Al-MoS_2	−2.33	−3.43	Zhang et al., 2018

In another instance, Qian et al. researched the adsorption property of H_2S and SO_2 on the Pt-decorated MoS_2 and found that Pt-MoS_2 showed a strong interaction with gas molecules due to the strong chemical activity of with Pt atom. The adsorption energy of H_2S and SO_2 molecules adsorbed on Pt-MoS_2 was −1.465 and −1.584 eV, respectively, suggesting the occurrence of strong chemisorption in the contact surfaces. The charge transfer amount between H_2S and Pt-MoS_2 was up to 0.302 e, which is much higher than that of SO_2 (0.036 e). The results indicated that Pt-MoS_2 exhibited an excellent adsorption property for H_2S gas (Qian et al., 2019). Wei et al. reported the response behavior of Ni-MoS_2 towards SF_6 typical decomposition products: SO_2 and H_2S. The different adsorption sites for the SO_2 and H_2S on Ni-MoS_2 surface were designed to find the site of optimal adsorption energy. The result of SO_2 and H_2S was −1.382 and −1.319 eV, respectively, indicating the strong chemical interaction between the Ni-doped MoS_2 monolayer and two kinds of gases (Wei et al., 2018). Gui et al. reported that Si-doped MoS_2 were used to investigate its adsorptive properties to H_2S and SOF_2, and found that the most stable doping site were above the S atom. The adsorption energy was −0.68 eV when H_2S adsorbed on Si-MoS_2, while pristine MoS_2 was only −0.17 eV. The adsorption energy of SOF_2 adsorbed on Si-MoS_2 reached −3.63 eV, which was much higher than the −0.01 eV of the pristine MoS_2 adsorption system. The results provided that the adsorption capacities of pristine MoS_2 for H_2S and SOF_2 gases could be greatly improved by doping them with a nonmetallic atom (Gui et al. 2019). Li et al. selected the Pd atom as the dopant to modify the surface of the MoS_2 monolayer in the latest study, and an adsorbent with higher properties for the adsorption of SOF_2 and SO_2F_2 gases was obtained on this basis. In addition, the double gas molecules could still be stably adsorbed on the surface of Pd-MoS_2, indicating the feasibility of the adsorbent (Li et al. 2020).

In the above, the adsorption of H_2S and SO_2 molecules in different systems have been discussed in detail. The simulation results of H_2S and SO_2 molecules adsorption are in **Table 1**. These values may be obtained by different DFT functions. Compared with the adsorption construction of a pristine MoS_2 system, the introduction of novel elements promotes the surface chemical activity of the MoS_2 system. In addition, the addition of dopants enhances the affect of orbital hybridization between the MoS_2 monolayer and gas molecules, and facilitates the electronic transfer. The

adsorption capacity of the modified materials to the goal gas will be further improved, when the dopant is suitable (Zhang et al., 2017a).

Experimental analysis about MoS_2-based sensors

At present, there are few experimental studies on the detection of SF_6 decomposed byproducts, the few that do mainly focus on the H_2S, SO_2, and CO gases (Wang et al., 2019a; Zhou et al., 2019). Park et al. prepared a MoS_2 gas sensor modified with Pt nanoparticles with a low detection limit and high sensitivity for H_2S gas. The Pt-MoS_2-based sensor reduced the minimum detection concentration of H_2S gas to 5 ppm, which was much lower than that of the pure MoS_2 sensor (30 ppm) (Park et al., 2018). The Pt-MoS_2 film structures were formed by the introduction of Pt nanoparticles with ultra-small diameters, which could distinctly improve the performance of sensors. The Ni-doped MoS_2 nanoflower synthesized by Zhang et al. displayed a faster and higher response to 5 ppm SO_2 gas (Ra/Rg = 14.75) at room temperature. The main reason was that the richer porosity in the nanoflower structures provided sufficient adsorption sites for SO_2 gas (Zhang et al., 2017b). Hierarchical MoS_2 nanospheres assembled from nanosheets fabricated by Zhou et al. exhibited high properties to CO. The response value of the gas sensor to 500 ppm CO reached 92.6 at 230°C. Besides, this sensor had almost no response to other gases when the operation temperature was higher than 200°C, indicating the outstanding selectivity toward CO gas (Zhou et al., 2018c). The experimental results show that these unique nanostructures can enhance the gas-sensing performance, which is attributed to the increase of oxygen vacancies and the promotion of gas adsorption-desorption efficiency. Although some advancements have been made in the detection of SF_6 decomposed products, more high-accuracy experiments are needed for other decomposition gases such as SOF_2 and SO_2F_2.

Gas sensing mechanism

The gas sensing mechanism of the MoS_2-based sensors to SF_6 decomposed products can be explained by the change of conductivity caused by the interaction between oxyanions (mainly O^-) on the material surface and target gas molecules. Firstly, the oxygen molecules in air will adsorb on the surface of semiconductor materials and capture electrons from the adsorption sites to form oxyanions. The formation of an electron depletion layer and the increase of resistance are caused by oxygen adsorption. Then, when sensors are placed in an environment of reductive gas, the test gas molecules react with oxyanions to release the electrons back to the surface of the material, resulting in the decrease of the electron depletion layer and the occurrence of conductivity change. The relevant reactions are depicted as follows (take H_2S gas as an example):

$$O_{2\,(g)} \rightarrow O_{2\,(ads)} \tag{3}$$

$$O_{2\,(ads)} + 2e^- \rightarrow 2O^-_{(ads)} \tag{4}$$

$$H_2S_{\,(g)} \rightarrow H_2s_{\,(ads)} \tag{5}$$

$$H_2s_{\,(ads)} + 3O^- \rightarrow SO_2 + H_2O + 3e^- \tag{6}$$

CONCLUSION

In this paper, we focused on the morphological characteristics and application of MoS_2 materials for the detection of SF_6 decomposed products in GIS. Firstly, partial reports of sensing properties of MoS_2 with various morphologies were concluded. Diverse MoS_2 structures presented relatively different sensing properties at specific operating temperatures, so it was possible to promote sensing performances of MoS_2 by simple surface morphology modification. With the increasing demand for sensor materials, simples and more convenient synthetic routes and more favorable morphology structures should be proposed. Next, it was shown that the selectivity and sensitivity of MoS_2 gas sensors could also be enhanced by the enlargement of the active surface area and the introduction of metal or non-metal elements based on formerly theoretical and experimental investigations. Then, the gas-sensing mechanism of the MoS_2 based sensors to SF_6 decomposed products was described by comparing the characteristics of material substrate and gas molecules. Although some developments have been obtained in theoretical research into SF_6 decomposed products, a large number of fundamental experiments are needed to further prepare MoS_2 sensors for practical industrial applications.

DATA AVAILABILITY STATEMENT

The raw data supporting the conclusions of this article will be made available by the authors, without undue reservation, to any qualified researcher.

AUTHOR CONTRIBUTIONS

All authors listed have made a substantial, direct, and intellectual contribution to the work, and approved it for publication.

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Conflict of Interest: Authors GQ, QP, DZ, SW, and BY were employed by the Electric Power Science Research Institute of Yunnan Power Grid Co., Ltd.