Morphological Characteristics of Molybdenum Disulfide and Current Application on Detecting SF₆ Decomposing Products

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MoS₂ 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. SF₆ 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 SF₆ gas will occur inevitably decompose due to partial discharge, resulting in the deterioration of the insulation performance of the equipment. Therefore, detecting SF₆ decomposition products is significant for the safe and stable operation of power systems. In this mini review, we start from the synthesis of various MoS₂ 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 MoS₂-based sensors for detecting SF₆ decomposition products. Finally, the future development in this field is proposed.

Keywords: molybdenum disulfide, morphological characteristics, SF₆ decomposing products, sensing application, gas insulated switchgear

INTRODUCTION

Sulfur hexafluoride (SF₆) 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 SF₆ gas into various sulfur fluorides, including H₂S, SO₂, SO₂F₂, and SOF₂ 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 SF₆ (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 SF₆ decomposed gas (Zhou et al., 2018a; Chen et al., 2018).
Given this, various 2-D nanomaterials such as carbon nanotube (CNT), graphene, and molybdenum disulfide (MoS₂) have been synthesized by different methods (Zhou et al., 2018e; Choi et al., 2020). As an n-type semiconductor material with wide band gap, MoS₂ 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 MoS₂, 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 SF₆ 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 MoS₂ nanostructures are of great significant to discuss. This mini review summarizes the morphological features and sensing applications of MoS₂, especially for detecting SF₆ decomposed products.

**Morphology and analysis of MoS₂**

MoS₂ 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 MoS₂ 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; Bhakhari et al., 2019). Kang et al. demonstrated vertical MoS₂ nanoflakes (shown in Figure 1A) fabricated on SiO₂/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 NO₂ gas. The minimum concentration of the NO₂ detection was 0.15 ppm at room temperature (Kang et al., 2017). Tu et al. synthesized hierarchical MoS₂ 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 MoS₂ 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 MoS₂ 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 MoS₂ 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,
MoS₂ SENSOR FOR SF₆ DECOMPOSING PRODUCTS

Theoretical calculations about MoS₂-based sensors

In order to analyze and investigate the adsorption process between SF₆ decomposed gases and MoS₂-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:

$$E_{ads} = E_{MoS2/gas molecule} - E_{MoS2} - E_{gas molecule}$$  \hspace{1cm} (1)

$E_{MoS2/gas molecule}$ is the systemic energy after reaction, $E_{gas molecule}$ and $E_{MoS2}$ signify the energy of gas molecule and the full energies of the MoS₂ before the reaction, respectively (Wang et al., 2019c). The negative value of $E_{ads}$ 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 MoS₂ system is defined by Eq. 2:

$$Q_t = Q_a - Q_b$$  \hspace{1cm} (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 MoS₂-based system to gas molecules.

The adsorption processes between gas sensing materials and SF₆ 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 SO₂ molecules on MoS₂ monolayers in the aspects of charge transfer, band structures, adsorption energy, and charge density differences. They found that SO₂ 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 MoS₂ monolayers and target gas molecules, and the adsorption of SO₂ changed the electronic properties of MoS₂ monolayer (Abbasi and Sardroodi 2019). Chen et al. theoretically discussed the adsorption behavior of five types of SF₆ decomposing products (H₂S, HF, SO₂, SOF₂, and SO₂F₂) on the MoS₂ monolayer by employing the NEGF combined with DFT method. Among the five types of gas molecules, MoS₂ monolayer had the best adsorption performance for SO₂ caused by the special electronegativity (Chen et al., 2019a).

In another instance, Qian et al. researched the adsorption property of H₂S and SO₂ on the Pt-decorated MoS₂ and found that Pt-MoS₂ showed a strong interaction with gas molecules due to the strong chemical activity of with Pt atom. The adsorption energy of H₂S and SO₂ molecules adsorbed on Pt-MoS₂ was –1.465 and –1.584 eV, respectively, suggesting the occurrence of strong chemisorption in the contact surfaces. The charge transfer amount between H₂S and Pt-MoS₂ was up to 0.302 e, which is much higher than that of SO₂ (0.036 e). The results indicated that Pt-MoS₂ exhibited an excellent adsorption property for H₂S gas (Qian et al., 2019). Wei et al. reported the response behavior of Ni-MoS₂ towards SF₆ typical decomposition products: SF₆ and H₂S. The different adsorption sites for the SO₂ and H₂S on Ni-MoS₂ surface were designed to find the site of optimal adsorption energy. The result of SO₂ and H₂S was –1.382 and –1.319 eV, respectively, indicating the strong chemical interaction between the Ni-doped MoS₂ monolayer and two kinds of gases (Wei et al., 2018). Cui et al. reported that Si-doped MoS₂ were used to investigate its adsorptive properties to H₂S and SOF₂, and found that the most stable doping site were above the S atom. The adsorption energy was –0.68 eV when H₂S adsorbed on Si-MoS₂, while pristine MoS₂ was only –0.17 eV. The adsorption energy of SOF₂ adsorbed on Si-MoS₂ reached –3.63 eV, which was much higher than the –0.01 eV of the pristine MoS₂ adsorption system. The results provided that the adsorption capacities of pristine MoS₂ for H₂S and SOF₂ 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 MoS₂ monolayer in the latest study, and an adsorbent with higher properties for the adsorption of SOF₂ and SO₂F₂ gases was obtained on this basis. In addition, the double gas molecules could still be stably adsorbed on the surface of Pd-MoS₂, indicating the feasibility of the adsorbent (Li et al. 2020).

In the above, the adsorption of H₂S and SO₂ molecules in different systems have been discussed in detail. The simulation results of H₂S and SO₂ molecules adsorption are in Table 1. These values may be obtained by different DFT functions. Compared with the adsorption construction of a pristine MoS₂ system, the introduction of novel elements promotes the surface chemical activity of the MoS₂ system. In addition, the addition of dopants enhances the affect of orbital hybridization between the MoS₂ monolayer and gas molecules, and facilitates the electronic transfer. The

| SF₆ Decomposing products | System      | $E_{ads}$ (eV) | $Q_t$ (e) | References               |
|-------------------------|-------------|---------------|----------|--------------------------|
|                         | H₂S         | –0.22         | 0.02     | Chen et al., 2019a       |
|                         | SO₂         | –0.68         | 0.16     | Gui et al., 2019          |
|                         | Pt-MoS₂     | –1.319        | 0.254    | Wei et al., 2018          |
|                         | Ni-MoS₂     | –1.465        | 0.302    | Qian et al., 2019         |
|                         | Al-MoS₂     | –1.584        | 0.036    | Qian et al., 2019         |
|                         | Si-MoS₂     | –0.30         | –0.04    | Chen et al., 2019a        |
|                         | Si-MoS₂     | –1.382        | –0.016   | Wei et al., 2018          |
|                         | Si-MoS₂     | –1.584        | –0.016   | Qian et al., 2019         |
|                         | Al-MoS₂     | –2.33         | –3.43    | Zhang et al., 2018        |
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$_2$S, 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$_2$S gas. The Pt-MoS$_2$-based sensor reduced the minimum detection concentration of H$_2$S 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$_2$F$_2$.

### 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$_2$S gas as an example):

$$O_2 (g) \rightarrow O_2(ads)$$  \hspace{1cm} (3)

$$O_2(ads) + 2e^- \rightarrow 2O^-(ads)$$  \hspace{1cm} (4)

$$H_2S (g) \rightarrow H_2S(ads)$$  \hspace{1cm} (5)

$$H_2S(ads) + 3O^- \rightarrow SO_2 + H_2O + 3e^-$$  \hspace{1cm} (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.

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