Study on the gas sensitivity of vanadium-doped molybdenum disulfide to mustard gas

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Abstract. As a graphene-like material, molybdenum disulfide has similar properties to graphene, but due to its excellent properties such as adjustable band gap, molybdenum disulfide has a broader application in many aspects (such as gas sensors). With the deepening of research, molybdenum disulfide cannot fully meet the needs of researchers due to defects and other reasons. Therefore, researches on doping and compounding of molybdenum disulfide have gradually attracted attention. At present, most of the research on gas sensitivity has focused on harmful gases (such as nitrogen dioxide, ammonia and carbon monoxide, etc.). There are few studies on the erosive chemical toxic mustard gas. In this paper, vanadium-doped molybdenum disulfide were prepared based on chemical vapor deposition, and the gas-sensitive response of vanadium-doped molybdenum disulfide to mustard gas was studied.

Keywords: Molybdenum disulfide, vanadium doping, mustard gas, gas sensitivity.

1 Introduction

Mustard gas was one of the main chemical warfare agents developed and used during the First World War, and there are still large stocks in some countries[1,2]. Pure mustard gas is a transparent, colorless liquid with almost no odor. Some impurities give the mustard gas a greasy appearance and the typical smell of garlic. Mustard gas is almost insoluble in water, but has good solubility in alcohol and organic solvents. Its freezing point is 14.4℃ and its boiling point is between 215 and 217℃[3]. Mustard gas is a foaming agent that can cause skin blisters, respiratory tract damage, eye disease, and bone marrow suppression. Despite a lot of research work in the past 90 years, no specific mustard gas antidote has been discovered[4].

In recent years, there have been reports of terrorist attacks and major public emergencies around the world. Our country has a large population and densely populated

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areas, and its ability to defend against chemical terrorist attacks is relatively weak. Once a terrorist attack occurs, social stability and economic development will be severely damaged. In addition, incidents of mustard gas abandoned in China by the Japanese invaders have repeatedly occurred, causing serious physical, mental and spiritual damage to the Chinese people. Therefore, rapid and accurate detection of trace amounts of mustard gas is an urgent question.

Chemical agent sensor has become an important means of chemical agent analysis and detection. There are many types of sensing principles, including ion mobility spectroscopy, flame photometry, semiconductors, etc. Among them, the resistive semiconductor gas sensor has attracted much attention because of its excellent sensing performance, simple preparation process and low cost. Among them, the resistive semiconductor gas sensor has attracted much attention because of its excellent sensing performance, simple preparation process and low cost. The sensitivity of the sensor depends on the adsorption between the surface of the material and the gas molecules.

In 2004, Novoselov and Geim of the University of Manchester in the United Kingdom successfully peeled off single-layer graphene using micromechanical peeling method[5]. Since then, two-dimensional materials have become a hot spot in the field of materials science due to their extremely large specific surface area. With the continuous deepening of materials science research, new graphene-like materials transition metal chalcogenides have gradually entered the field of vision of researchers. Transition metal sulfides also show their unique physical and chemical properties. The compound has great application prospects in many fields such as optoelectronic devices, catalysis, energy conversion, storage and sensing [6-10]. All the constituent atoms of a single-layer transition metal sulfide are exposed to the surrounding environment. Its large specific surface area provides good conditions for the adsorption of gas molecules on the surface. The sheet layer can be used as an electron donor or acceptor. The transfer between the two-dimensional sheet and the adsorbed gas molecules can change the resistance and carrier density of the single-layer transition metal sulfide. This is the principle of its application in gas sensors[11,12].

Among transition metal sulfides, molybdenum disulfide (MoS_2) is the earliest and most widely studied material [13-14]. A large number of previous experiments have shown that MoS_2 is an ideal transition metal sulfide that can be used as a gas-sensing material for chemical sensors[15-17]. However, when intrinsic MoS_2 is exposed to the air, its surface easily adsorbs oxygen, resulting in a significant decrease in its carrier concentration and carrier mobility, resulting in unsatisfactory gas sensitivity[18]. Therefore, the intrinsic MoS_2 gas sensor device needs to work in a vacuum or inert atmosphere to maximize its excellent gas sensitivity characteristics, which severely limits the application of the intrinsic MoS_2 gas sensor device in military field poison detection. Doping the intrinsic molybdenum disulfide with other metal atoms can make up for its original defects, effectively reduce the combined ratio of the material and the oxygen in the gas to be measured, and significantly improve the sensing performance[19,20]. This article intends to dope V element into MoS_2 to solve the problems of low response and poor stability of two-dimensional MoS2 in the air, and initially explore the response of V-doped molybdenum disulfide (V-MoS_2) to mustard gas.

2 Experimental section

2.1 Material preparation

The gas-sensitive materials in this study are all prepared by chemical vapor deposition. Pure MoS_2 is obtained by vaporizing molybdenum trioxide powder and sulfur powder at

high temperature and finally depositing on the substrate. The preparation method of the two-dimensional MoS_2 material doped with V is similar to the above process. But the difference is that in the preparation process of the doping material, a certain amount of VO_2, MoO_3 and KCl must be thoroughly ground and mixed in a mortar to form a uniformly mixed solid of niobium oxide and molybdenum oxide as the metal source for growth. The addition of KCl is to increase the volatilization rate of the metal source into the gas phase. The temperature of the sulfur sublimation zone is 180°C, the temperature of the deposition growth zone is 650°C, and the growth pressure is 2000Pa. The deposition time is 15min to obtain the V-doped MoS_2 material. The schematic diagram of the process is shown in Figure 1.
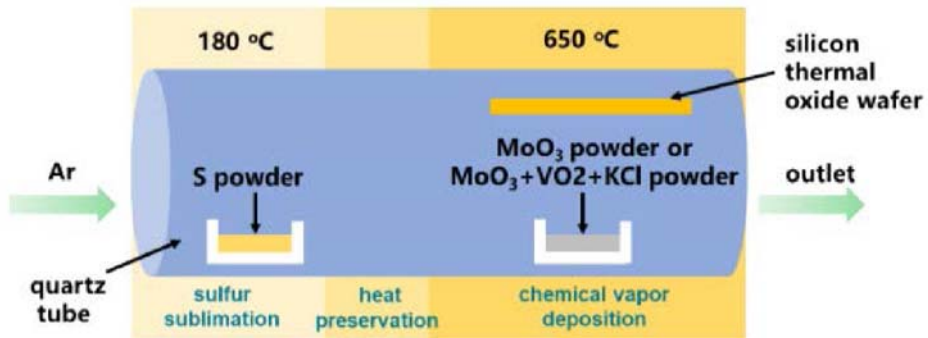

Figure 1. Schematic diagram of preparation of V- MoS_2 by chemical vapor depositio

2.2 Characterizations

The most intuitive characterization methods of two-dimensional layered materials are various microscopes, including scanning electron microscopy, atomic force microscopy, etc. In this paper, the morphology of the samples was characterized by scanning electron microscopy (SEM), and the thickness of the films was identified by atomic force microscopy (AFM) and Raman spectroscopy (Raman). The relative content of each element in the sample was determined by EDS. X-ray photoelectron spectroscopy (XPS) is an important surface analysis method, which can determine the composition and chemical valence state of the surface elements through the electron binding energy. All XPS spectra were corrected by C 1s (284.8 EV).

2.3 Fabrication of gas sensor

In order to facilitate the application of electrical signals to the MoS_2 thin-film gas sensor and accurately measure its surface resistance, it is necessary to pre-make the lead electrodes on the silicon substrate. Firstly, a mask of interdigital shape is pasted on the surface of the cleaned and dried substrate. The interdigital electrode mask used in the experiment is made of 0.1 mm thick alloy sheet by laser. Then, the substrate covered with the mask was put into the vacuum chamber of the magnetron sputtering equipment. The metal gold was used as the target and argon as the working gas. Under the conditions of argon flow rate of 25 ml/min, substrate temperature of 25°C, background vacuum less than 4×10^{-4} Pa and sputtering pressure of 2.0 Pa, platinum interdigital electrode with thickness of 0.1-0.3 μm was obtained.

2.4 The occurrence of dynamic air currents

Mustard gas (purity more than 98%) is provided by The Institute of NBC Defense. The method is as follows: a certain amount of liquid agent is injected into the volatilization chamber, the orifice plate is covered and the upper cover is tightened, and placed in the poison generator. Adjust the cold trap to keep the agent in the liquid state in the generator. Through the gas mass flow controller, the constant air flow is introduced, and the poison vapor diffused from the volatilization chamber is carried out, and the stable poisoned gas flow is formed after dilution. In the process of the experiment, the temperature of cold trap, the pore size in the center of volatile orifice plate and the flow rate and ratio of purge and dilution gas flow can be adjusted to produce dynamic agent gas flow with different concentrations.

2.5 Gas sensing measurements

Connect the gas circuit, power line and data transmission line of the detection system, turn on the sensor power supply and the upper computer control software, realize the signal connection, first connect the dry clean air into the detection room, and make it interact with the two-dimensional MoS_2 sensitive film on the sensor array. After the signal generated is counted by the resistance value acquisition device, it is sent to the computer for recording by the recording software, and the air sensor is obtained The working curve of the parts in the clean air flow. After the baseline is stable, the air will be switched to the gas flow with known concentration of mustard gas, and then switch to air after a certain time. When the resistance value of load is restored to the initial value or near the initial value, the toxic air flow shall be injected again, and the above process shall be repeated several times to ensure that the sensitivity fluctuation of repeated test of response sensitivity under the same test condition is less than 10%. Use the self-built intelligent gas sensitivity analysis system to test the gas sensitivity performance and study the sensitivity of the gas sensor to the mustard gas detection S:

$$S(\%) = 100 * \frac{\Delta R}{R_0} = 100 * \frac{R_g - R_0}{R_0} \qquad (1)$$

Among them, R_0 and R_g are the resistance values of the thin film gas sensor in the air and the gas flow of the sample to be tested.

3 Results and discussion

3.1 Structure and morphology

3.1.1 Scanning electron microscope

Figure 2 shows the SEM image of V-MoS_2. It can be seen that the V-doped samples have the needle like morphology.
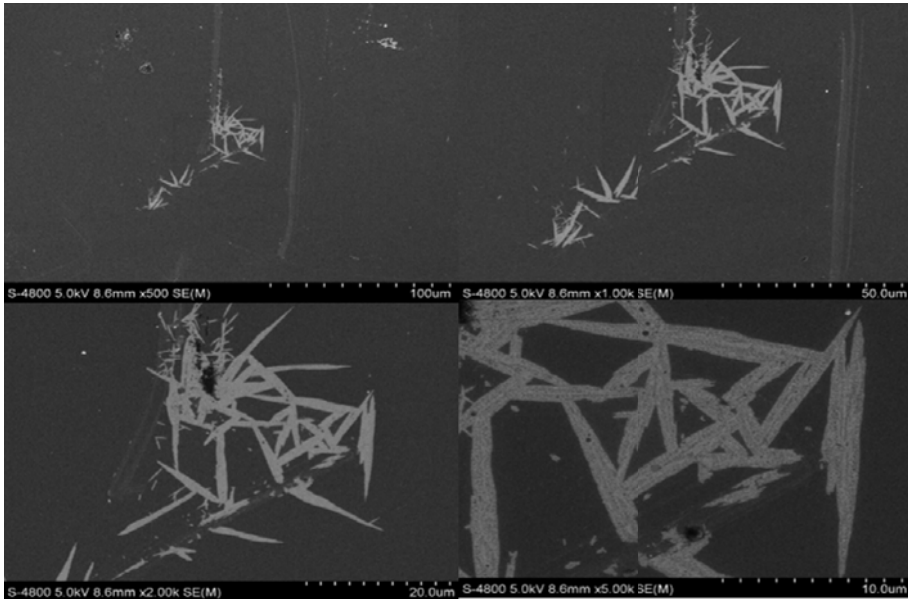
Figure 2. SEM of V-MoS$_2$

3.1.2 Atomic force microscope

As shown in Figure 3 is the height profile of V-MoS$_2$ with few layers of MoS$_2$. It can be seen that the thickness of V-MoS$_2$ sample sheet is about 3.8 nm, which is consistent with the thickness of 4-5 layer MoS$_2$ material.
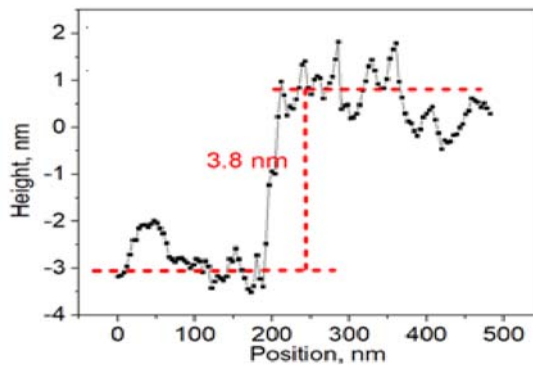

Figure 3. Quantitative height profile corresponding to AFM images of V-MoS$_2$ sample

3.1.3 Raman

The Raman spectra of MoS$_2$ before and after V doping are shown in Figure 4. It can be seen from the figure that the introduction of V has little effect on the position of the in-plane vibration peak E_{2g}^1 and the interlayer vibration characteristic peak A_{1g} of S atom, and the wave number difference between the two characteristic peaks has no obvious change, which indicates that the addition of a small amount of V has little effect on the structure of MoS$_2$ film. In the same way, it can be seen from the Raman spectra that the

intensity ratio of the in-plane vibration peak E_{2g}^1 of S atom to that of the interlayer vibration peak A_{1g} of S atom decreases after introducing a small amount of V.
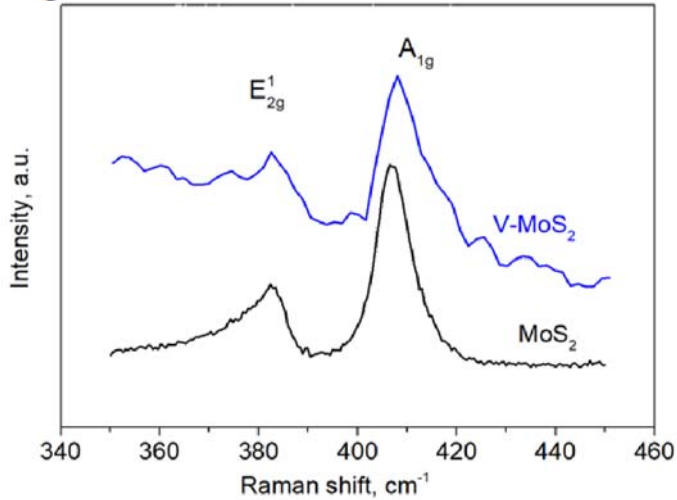

Figure 4. Raman of MoS_2 and V-MoS_2 samples

3.1.4 Energy Dispersive X-Ray Spectroscopy (EDS)

EDS is a method to determine the relative content of elements in the sample by analyzing the characteristic X-ray wavelength and intensity of the sample. Figure 5 is the SEM-EDS mapping diagram of V-MoS_2 sample. It can be seen that the distribution of Mo, S and V in the sample is highly uniform, which also confirms that V element can be well doped into two-dimensional MoS_2 by chemical vapor deposition.
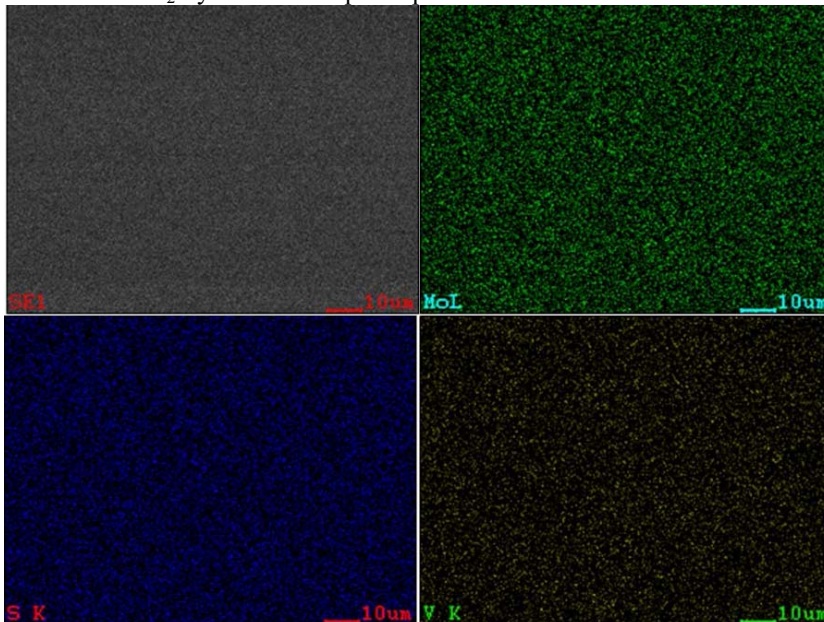

Figure 5. SEM-EDS mapping diagram of V-MoS_2

3.1.5 X-ray photoelectron spectroscopy (XPS).

Figure 6(a) shows the full XPS spectrum of V-MoS$_2$ sample. It can be seen that the characteristic peaks of the main elements in the samples are very obvious, and are consistent with the XPS spectra of MoS$_2$. Figure 6(b) shows the high resolution scanning spectrum of V in the narrow region of 2p orbit in V-MoS$_2$ sample. It can be seen that there are characteristic peaks of VS$_2$ at 514.36 eV and 521.86 eV in this region. Based on the above XPS results, it is shown that V-MoS$_2$ materials can be successfully synthesized by vapor deposition method.
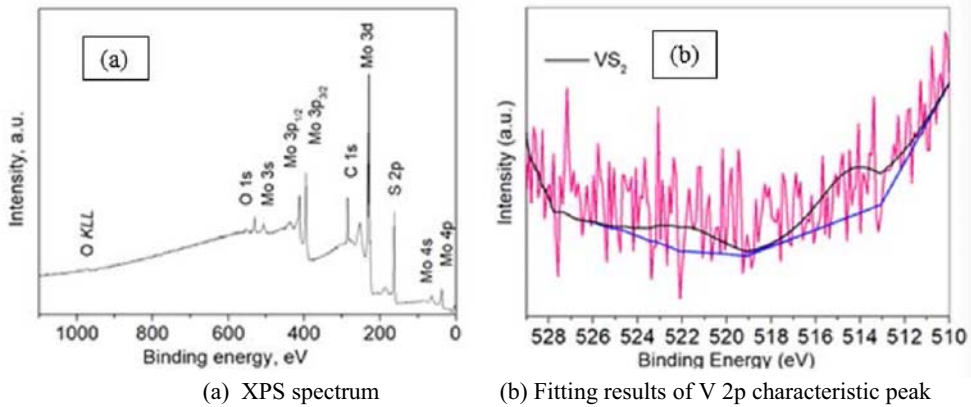

(a) XPS spectrum (b) Fitting results of V 2p characteristic peak

Figure 6. X-ray photoelectron spectroscopy of V-MoS$_2$

3.2 Gas sensing properties

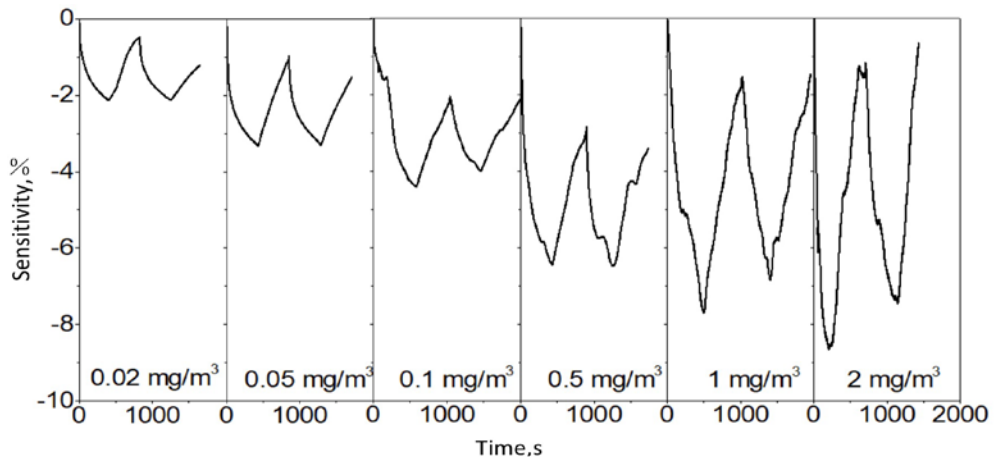### *3.2.1 Response of different concentrations of mustard gas*

Figure 7. Comparison of response curves of V-MoS$_2$ in different concentrations of mustard gas

The response curves of V-MoS$_2$ samples to different concentrations of mustard gas were obtained by gradually reducing the concentration of mustard gas in the contaminated gas stream. The results are shown in Figure 7. It can be seen that in different concentrations of mustard atmosphere, with the extension of response time, the response sensitivity of the materials first decreased rapidly and then tended to be flat. When the concentration of

mustard gas is low, the response curve is very smooth, while when the concentration of mustard gas is high, the response curve appears noise, which may be due to the uneven local gas mixing in the high concentration mustard gas experiment. In view of the actual needs of the detection of toxic agents, we focused on the response performance of sensitive materials at low concentrations. When the concentration of mustard gas was 0.02 mg/m^3 (2.8 ppb), the response curve was still clear, and the response degree was 2.13% under the experimental conditions.

3.2.2 Repeatability of response to mustard gas

In order to test the repeatability of response of V-MoS$_2$ sensitive material, mustard gas at the same concentration was continuously measured for 5 times. The results show that V-MoS$_2$ has good repeatability for 5 times of mustard gas detection of 0.1 and 2 mg/m^3, and the sensitivity fluctuation is less than 10% after deducting the baseline fluctuation factor, which indicates that this kind of material has good repeatability detection.
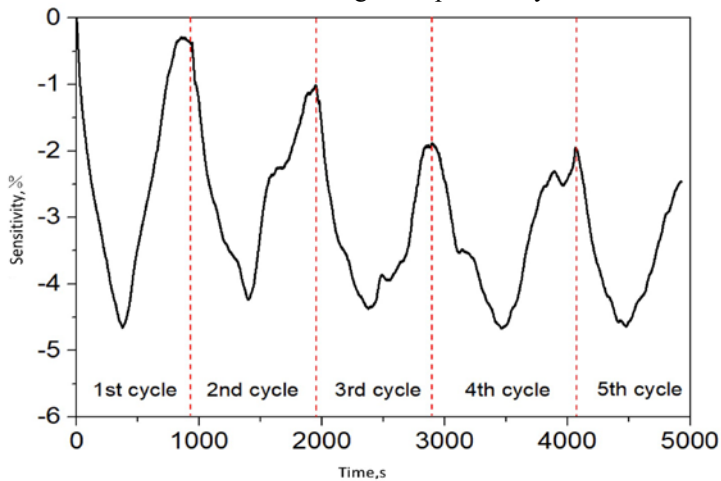

Figure 8. Repeatability of response of V-MoS$_2$ to 0.1 mg/m^3 mustard gas

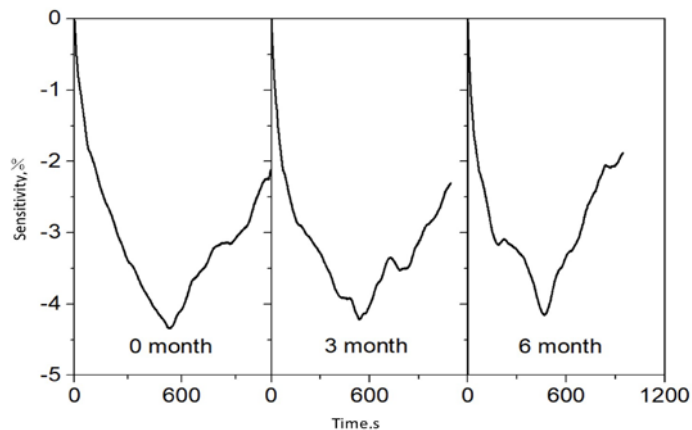### 3.2.3 Stability of response to mustard gas

Figure 9. Response stability of V-MoS$_2$ to 0.1 mg/m^3 mustard gas

After the sensor is placed for a period of time, its response performance to 0.1 mg/m^3 mustard gas is tested, and the results are shown in Figure 9. It can be seen from the figure that the performance of mustard gas detection has no obvious change after the sensor is placed for 3 months and 6 months, and the change of response amplitude SM is less than 10%, which indicates that this kind of sensitive material has good stability in air.

4 Conclusions

In this paper, a few-layer V-doped two-dimensional MoS2 was successfully prepared by chemical vapor deposition, and a sensor for the erosive agent mustard gas was developed using it as a sensitive material. The experimental results show that the V-MoS$_2$ sample has a high response to mustard gas, and shows good repeatability and stability in mustard gas detection. In this experiment, the detection limit of the two-dimensional V-MoS$_2$ low-layer material for mustard gas is as low as 0.02mg/m^3, which can meet the requirements for on-site identification and detection of mustard gas at trace levels. This indicates that V-doped molybdenum disulfide is expected to be a gas-sensitive material for the mustard gas sensor of erosive agent.

Acknowledgments

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