Research Progress of MoS₂ Composite rGO Material in Gas Sensor

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Abstract. Since the successful preparation of single-layer graphene in 2004, two-dimensional materials have gradually become one of the research hotspots in the field of materials science. However, due to the inevitable defects of intrinsic two-dimensional materials, researchers began to explore how to obtain more excellent two-dimensional materials. In this paper, the basic properties, preparation methods and application in gas sensors of MoS₂/rGO composites are reviewed. This paper has a certain reference value for the research of two-dimensional materials used in gas sensors.

1 Introduction

With the further promotion of industrialization and the rapid development of economy, toxic, harmful, flammable and explosive gases often appear in people's daily life and production activities, and there are often major safety accidents, causing serious damage to social stability and economic development. On March 20th, 1995, the Japanese cult created the appalling 'sarin incident in Tokyo subway', resulting in 12 deaths and more than 5500 poisoning. On August 12th, 2015, Ruihai company, located in Tianjin port, Binhai New Area, Tianjin, suffered a combustion and explosion accident, resulting in 165 deaths, 8 missing and 798 injured, with a direct economic loss of 6.866 billion yuan. China's population ranks first in the world, and the population density in most areas far exceeds the average level of the world. Therefore, it is relatively difficult to defend against biochemical terrorist attacks. At the same time, with the continuous improvement of China's comprehensive national strength, China's world status is also constantly improving, and various large-scale international activities have been held in our country. Without a strict security system, we cannot shoulder this heavy responsibility. In recent years, the surrounding security situation has not been underestimated. It is particularly important to prevent terrorist attacks, extremism and major emergencies. Chemical weapons protection, anti-chemical terrorism and chemical disaster treatment together constitute the major practical needs of national defense and national security. Therefore, rapid, accurate and trace detection of toxic and harmful gases is very important. In this paper, the research progress of MoS₂/rGO materials in gas sensors is reviewed, which will lay a foundation for the next research.

2 Electrochemical properties

MoS₂ has been widely studied in the field of gas sensors. However, due to its poor relative conductivity and low structural strength, its development as a raw material for gas sensors is limited to a certain extent. It is difficult for intrinsic MoS₂ to overcome its defects in conductivity and structural strength, so it is difficult to further expand the application prospect of intrinsic MoS₂. The layered composite structure composed of MoS₂/rGO materials effectively improves the gas sensing performance of the materials^[1-5]. The prepared MoS₂ composite graphene can be encapsulated in the button cell by the cell preparation process to characterize its electrochemical performance. The characterization methods include cyclic voltammetry test, galvanized charge discharge test and AC impedance test.

Cyclic voltammetry is one of the most commonly used methods to study the electrochemical performance of batteries. By controlling the electrode potential at different rates and scanning with a triangular waveform one or more times over time, the 'electrochemical spectrum' can be obtained by recording the curve of the current changing with the electrode potential during the cycle. According to the curve, the reversibility of the electrode reaction and the possibility of phase boundary absorption can be judged, and the properties of coupling reaction^[6]. Constant current charge discharge test takes voltage as response signal and current as control signal to charge or discharge the battery under test through constant current density. At the same time, the change of battery voltage with time is analyzed, and then the reaction process of its electrode is studied, and the electrochemical performance of the battery is analyzed. AC impedance test is to apply small amplitude AC voltage with different frequencies to the research electrode, so that the electrode potential is slightly

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disturbed near the equilibrium electrode potential. After the electrode system is disturbed, the amplitude and phase angle of the corresponding current signal will be generated. AC impedance spectrum can be obtained by recording the changes of the disturbance signal with time and the response signal with time.

The electrical properties of the composite are better than pure MoS₂ and graphene, mainly for the following reasons: firstly, both MoS₂ and graphene have high conductivity, so the conductivity of MoS₂ Composite graphene is correspondingly high; secondly, because graphene is a porous material, it can increase the storage capacity of lithium ion and promote the diffusion of electrolyte in the materials. In addition, MoS₂ is an X-M-X sandwich structure, which shortens the transmission distance of lithium ion and greatly improves the rate performance of materials^[7-9]. After high rate charge and discharge, the current density can return to 100mA·g⁻¹ again, and the capacity can be maintained at 1203.6 mAh·g⁻¹, which is basically the same as the original data, indicating that the structure of the composite is very stable and can withstand repeated charge and discharge of different rate current^[10].

The electrochemical characterization results show that the unique properties of graphene can be effectively utilized, the complementary properties of MoS₂ and graphene can be realized, the electric storage capacity and stability of the composite can be enhanced, the practical application value of graphene can be expanded, the surface effect and synergistic effect of the composite can be exerted, and the comprehensive properties of the composite can be significantly improved^[11].

3 Preparation of Materials

After consulting literature in related fields, it is found that there are three main methods to prepare MoS₂/rGO materials, including hydrothermal synthesis, chemical vapor deposition and solution self-assembly. The following will be classified and summarized according to the preparation methods of MoS₂ composite graphene materials.

3.1 Hydrothermal synthesis

Hydrothermal synthesis is an effective method for the production of MoS₂/rGO materials with high quality. At first, MoS₂ was formed by mixing Sodium molybdate (Na₂MoO₄) and Thiourea (CH₄N₂S) under high temperature and high pressure. At the same time, graphene oxide gradually lost oxygen containing group and converted it into reduced graphene oxide, and formed a close composite structure with MoS₂.^[2,12] The graphene oxide prepared by the modified Hummers method was used as the template for hydrothermal reaction by Chang K et al.^[13-14] Na₂MoO₄ and CH₄N₂S were used as the precursor of MoS₂, and the reaction was fully performed for 24 hours at 240°C. Due to the static and electric power, molybdate ion will be absorbed on the surface of graphene oxide, graphene oxide will be reduced and formed a close

composite structure with MoS₂, and finally the close layered structure of MoS₂/rGO materials can be obtained. The schematic diagram of composite materials synthesis is shown in Fig.1(a), and Fig.1(e) is a structural diagram.

Figure 1. (a) Schematic diagram of the in situ synthesis of MoS₂/GNS; (b) Schematic illustration of the microstructure of MoS₂/GNS.^[13]

The hydrothermal synthesis method can prepare MoS₂ Composite graphene materials with compact structure, which can give full play to the excellent electrical conductivity and structural support of graphene, and fully ensure the related properties of the composite materials. However, hydrothermal synthesis also has its inherent defects: one is that the prepared MoS₂ has disordered lattice and poor crystallinity; the other is that it can not directly and effectively control the proportion and yield of the two components in the product, which has many adverse factors on the performance and morphology control of the composite.

3.2 Chemical vapor deposition

Chemical vapor deposition (CVD) is an effective method to obtain two-dimensional composites with regular structure, and regular structure is an important guarantee for gas sensing properties of MoS₂/rGO materials. MoS₂ and reduced graphene oxide with two-dimensional lamellar structure can be prepared by CVD. The required structure can be obtained by changing the reaction conditions, and the properties of the composite can be improved^[15].

There are two ways to grow composite materials by CVD. The first is a two-step method: first, the precursor based on Mo is deposited on graphene substrate, and then sulfurized to obtain MoS₂/rGO materials; the second is one-step method: MoS₂/rGO materials are prepared on graphene substrate by gasification of transition metal Mo and S. MoS₂ films were prepared by thermal annealing in sulfur atmosphere. The size and thickness of MoS₂ films can be controlled by the size and thickness of Mo films. However, the MoS₂ films prepared by this method are usually multi-layer, so it is difficult to obtain single-layer sheet materials. Li, et al.^[16] used MoO₃ instead of Mo as raw materials, and believed that MoO₃ was reduced to form MoO_{3-x} intermediate, and then diffused to the substrate for further reaction with gaseous S powder. The size and thickness of MoS₂ can be controlled by controlling the reaction temperature, gas flow rate, Mo source, the distance between S source and substrate. CVD has strong controllability in the preparation of MoS₂/rGO materials with regular structure. However, CVD has low yield and harsh experimental conditions, which can not meet the needs of large-scale production.

3.3 Solution self assembly method

The above two methods have their own advantages and disadvantages in the preparation of MoS₂/rGO materials, but they have a common disadvantage that it is difficult to accurately control the reaction conditions and large-scale production. Compared with hydrothermal synthesis method and chemical vapor deposition method, MoS₂/rGO prepared by solution self-assembly method is easier to achieve large-scale preparation. In addition, the composition ratio and microstructure of MoS₂/rGO can be precisely controlled by selecting the size and number of layers of raw materials. In the preparation of MoS₂/rGO materials by solution self-assembly method, all kinds of raw materials need to be stably dispersed in the solvent to form a homogeneous suspension. Then, MoS₂ sheets stably dispersed in the solvent were obtained by liquid-phase ultrasonic exfoliation method and other methods, and the size of the nanosheets was screened by controlling the centrifugal time and rotating speed. At the same time, the water-soluble graphene oxide also met the conditions of solution self-assembly, thus forming MoS₂/rGO materials^[2]. Although this method can be used to prepare composites in large quantities, it is difficult for the reduced graphene oxide to disperse uniformly in the liquid phase again due to the fact that there is no kneeling, stacking or troubling phenomenon in the process of graphene oxidation followed by reduction.

4 Application of materials in gas sensors

Formaldehyde (HCHO) is a common harmful gas, which is closely related to people's daily life. HCHO can be detected in many newly decorated rooms and newly bought cars. Therefore, the HCHO gas sensor has always been the research focus of civil sensors. Xian Li, et al.^[17] used MoS₂/rGO materials for HCHO detection. A simple self-assembly method was used to prepare MoS₂/rGO based gas sensors on poly (naphthalene dicarboxylate) vinyl, and a flexible device for formaldehyde detection at room temperature was obtained. The sensing test results show that MoS₂/rGO based sensor has high sensitivity to HCHO and can detect ppm HCHO. In addition, MoS₂ composite reduced graphene oxide based sensors show higher sensitivity than pure reduced graphene oxide (rGO) sensors, which may be due to the enhancement of HCHO adsorption and electron transfer ability of two-dimensional materials after MoS₂ composite. In addition, different MoS₂ nanosheets were prepared by method, and their sensitivity to HCHO was compared. The results show that the sensitivity of MoS₂ nanosheets synthesized by hydrothermal method is higher, and the MoS₂ nanosheets synthesized by this method have rich defects, which lead to the improvement of the sensitivity of MoS₂/rGO based sensors, as shown in Fig.2.

Figure 2. Real-time sensing response curves (a) and (b) sensing response of the rGO/MoS₂-HT and rGO/MoS₂-CE sensors to 2.5-15.0ppm HCHO. Sensing response of the rGO sensor was included in figure 2(b) for comparison.^[17]

The rapid development of the chemical industry and the rapid consumption of energy lead to a large number of harmful gases in the atmosphere. The common harmful gases are nitrogen oxide (NO_x), ammonia (NH₃), hydrogen (H₂) and carbon monoxide (CO). Among these harmful gases, NO₂ and NH₃ will not only do harm to the environment, but also harm people's health, such as damaging the ozone layer, causing acid rain, causing pulmonary edema, etc. Neha kanaujiya, et al.^[18] synthesized petal like MoS₂ by hydrothermal method, and then prepared MoS₂ composite graphene materials. The research group explored the sensing properties of pure MoS₂ and its composite rGO materials at different temperatures and concentrations of NO₂. Results as shown in Fig.3, compared with pure MoS₂ sample, the response of composite sample was improved, and the response of composite sample to NO₂ concentration of 40ppm was about 23% at room temperature.

Figure 3. (a) I-V characteristics of MoS₂/rGO composite; (b) Response versus temperature graph for MoS₂ and MoS₂-rGO composite; (c) Responses of MoS₂ for different concentration of NO₂ gas at 40°C; (d) Response of composite for 40ppm NO₂ gas at room temperature.^[18]

H₂ is a kind of flammable and explosive gas, and serious casualties caused by H₂ explosion also occur from time to time. A Venkatesan et al.^[19] reported the sensing of H₂ by MoS₂/rGO materials. As shown in Fig.4, MoS₂/rGO materials show high sensitivity to H₂. It can respond to 200 ppm H₂ (15.6%) at 60°C. In addition, MoS₂/rGO has good selectivity for H₂. The response of the composite to H₂ is 2.9 times that of NH₃ and 3.5 times that of NO. The high sensitivity and selectivity of the composite to H₂ at lower operating temperature may be due to the structural integration of MoS₂ nanoparticles in the nano channels and graphene pores.

Fig.4 (a) response of reduced graphene oxide to 200 ppm and 500 ppm H₂ at different temperatures; (b) The response of the composites to 200 ppm and 500 ppm H₂ at different temperatures was studied; (c) The response of the composites to 200 ppm, 500 ppm H₂, NO and NH₃ at 60 °C was studied.^[19]

5 Conclusion

At present, the research of two-dimensional nano materials is very hot. Researchers are exploring different applications according to the excellent properties of two-dimensional nano materials. MoS₂/rGO materials can complement defects and are superior to pure graphene and pure MoS₂ in many aspects. In the aspect of gas sensors, many researchers have explored the sensitivity of composite materials to related gases, and the results show that the gas sensing performance of composite materials is better than that of pure graphene or pure MoS₂.

Most of the existing gas sensors are used to detect harmful gases in the atmosphere, such as nitrogen oxides, ammonia, formaldehyde and so on. If the composite gas sensor is used for the detection of trace chemical warfare agents such as mustard gas and sarin, it will be of great significance to China's national security and national defense construction. In addition, the detection limit of most gas sensors has reached ppm or even ppb level, but the selectivity is not satisfactory. If the gas sensor array is used to detect mixed gas vapor or aerosol, its unique two-dimensional response curve can be drawn, which is called 'fingerprint'. After learning and identifying by computer through neural algorithm, the selectivity of gas sensor will be greatly improved.

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